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QUALITY ASSURANCE PROJECT PLAN OPERATION, MAINTENANCE AND MONITORING PLAN

Summit National Superfund Site
Deerfield Township of Portage County, Ohio

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QUALITY ASSURANCE PROJECT PLAN OPERATION, MAINTENANCE AND MONITORING PLAN

Summit National Superfund Site
Deerfield Township of Portage County, Ohio

JULY 1994
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CONESTOGA-ROVERS & ASSOCIATES

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LIST OF ACRONYMS AND SHORT FORMS

BNA	-	Base-Neutral and Acid Extractable Compounds
°C	-	Degree Centigrade
CRA	-	Conestoga-Rovers & Associates
DQO	-	Data Quality Objective
GC	-	Gas Chromatography
GC/MS	-	Gas Chromatography/Mass Spectrometry
IU	-	Intermediate Unit
MS/DUP	-	Matrix Spike/Laboratory Duplicate
MS/MSD	-	Matrix Spike/Matrix Spike Duplicate
OEPA	-	Ohio Environmental Protection Agency
PCB	-	Polychlorinated Biphenyls
PE	-	Performance Evaluation
PPL	-	Priority Pollutant List
QA	-	Quality Assurance
QA/QC	-	Quality Assurance/Quality Control
QAPP	-	Quality Assurance Project Plan
QAS	-	Quality Assurance Section
QC	-	Quality Control
RPD	-	Relative Percent Difference
RPM	-	Remedial Project Manager
Site	-	Summit National Superfund Site
SNFT	-	Summit National Facility Trust
SOP	-	Standard Operating Procedures
SSIPL	-	Site-Specific Indicator Parameter List
SVOC	-	Semi-Volatile Organic Compounds
SW-846	-	SW-846, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods", 3rd Edition, November 1986
TAL	-	Target Analyte List
TCL	-	Target Compound List
USEPA	-	United States Environmental Protection Agency
USU	-	Upper Sharon Unit
VOC	-	Volatile Organic Compounds
WTU	-	Water Table Unit

QUALITY ASSURANCE PROJECT PLAN (QAPP)

PROJECT TITLE: Summit National Superfund Site
Operation, Maintenance and Monitoring Plan

PREPARED BY: CONESTOGA-ROVERS & ASSOCIATES (CRA)

Approved By: _____ Date:_____
Chairperson
Summit National Facility Trust
Gary Gifford

Approved By: _____ Date:_____
Project Manager - CRA
Jack Michels

Approved By: _____ Date:_____
QA/QC Officer -
Analytical and Field Activities - CRA
Steven Day

Approved By: _____ Date:_____
Project Manger - Accutest
Patricia Grieco

Approved By: _____ Date:_____
QA Officer - Accutest
Maria Ruschke

Approved By: _____ Date:_____
USEPA Region V
Remedial Project Manager
Anthony Rutter

Approved By: _____ Date:_____
USEPA Region V
Quality Assurance Reviewer

12.1 PROJECT DESCRIPTION

This QAPP has been developed for and is part of the long term Operation, Maintenance and Monitoring Plan (O&M Plan) for the Site. The project description is presented in Sections 1.0 and 2.0 of the O&M Plan.

The O&M Plan has been prepared pursuant to the requirements of the document "Statement of Work and Appendices to Statement of Work", Summit National Superfund Site, Deerfield Township of Portage County, Ohio printed on December 14, 1989 (Statement of Work).

The final effluent monitoring requirements presented in the QAPP have been prepared pursuant to the Substantive Permit for the Summit National Treatment Plant issued by the Ohio Environmental Protection Agency (OEPA) May 18, 1994 and discussions with OEPA and USEPA on May 19, 1994. Revised discharge limits for inorganic constituents were confirmed by CRA in correspondence dated November 29, 1996.

12.1.1 Site Background

A detailed Site background is presented in Section 1.0 of the O&M Plan.

12.1.2 Sampling Network and Rationale

The sampling network and rationale specified by the SOW is presented in Section 8.1 of the O&M Plan.

12.1.3 Project Objectives and Scope

The purpose of the O&M Plan is to provide operation, maintenance and monitoring guidelines for the Site during the period from completion of the remedial construction activities to termination of groundwater extraction, treatment and monitoring at the Site. This QAPP has been prepared in support of the O&M Plan to provide QA/QC procedures and requirements for the Consent Decree monitoring requirements specified in Section 8.1 of the O&M Plan to be performed during the long term operation, maintenance and monitoring of the Site. Specific objectives of the data collection activities include:

i) the annual collection and analysis of one surface water and sediment sample at the confluence of the south and east drainage ditches;

ii) the demonstration of hydraulic containment of Site-related contaminated groundwater in the Water Table Unit (WTU) and the Intermediate Unit (IU) by measurement and analysis of groundwater levels;

iii) the demonstration of reduction of the concentrations of Site-related contaminants in groundwater within the WTU and the IU to concentrations specified by the cleanup standards which are based on an individual 10^{-6} increased lifetime cancer risk for individual compounds and a comulative non-carcinogence Hazard Index (HI) less than 1 or background, whichever occurs first by analysis of groundwater samples;

iv) the demonstration that the hydraulic and water quality characterization in groundwater within the Upper Sharon Unit (USU) is not significantly impacted by the Site by measurement and analysis of groundwater levels and by analysis of groundwater samples;

v) the demonstration that water quality characteristics in local residential wells are not impacted by the Site by analysis of well water samples; and

vi) the demonstration of the effectiveness of the groundwater treatment system by measuring influent and effluent flow rates, chemical analysis of the treated water effluent and chemical analysis of the emissions from the vapor phase carbon adsorption vents.

The evaluation of the data collected will determine if the groundwater collection and extraction system is performing to its design criteria, whether the contingency measures outlined in Section 8.1.2.5 of the O&M Plan require implementation and at what point in time operation of the WTU and IU extraction systems may be terminated. In addition, compliance with final effluent requirements of the groundwater treatment system will be evaluated by the data.

The Statement of Work required that the final effluent be monitored for the Priority Pollutant List of parameters. However, the Substantive Permit issued by OEPA required that different parameters be monitored. The parameters required to be monitored, as presented in Table 12.4, were from the Target Compound List and Target Analyte List and not the Priority Pollutant List. Consequently, the methods to be used for the analysis of the final effluent will be consistent with the methods to be used for the analysis of the groundwater.

The OEPA discharge limits are presented in Table 12.4. Select metals discharge limits will be achieved by reporting to the laboratory's instrument detection limits and have been identified on the table with a footnote. This has been deemed acceptable by OEPA.

Consistent with the O&M Plan, a Site-specific indicator parameter list (SSIPL) was developed following the first full year of

groundwater monitoring and submitted to USEPA and OEPA for approval. The SSIPL was discussed with USEPA and OEPA on September 5, 1996 and confirmed by CRA in correspondence dated September 13, 1996. USEPA and OEPA approved the SSIPL in correspondence dated October 10, 1996 and October 18, 1996, respectively.

Groundwater samples collected from monitoring wells in the WIU, upper IU, lower IU, USU and from residential wells will be analyzed for SSIPL VOCs and metals analytes from the November 1996 monitoring event until the November 1999 monitoring event. In addition, during the November 1997 groundwater monitoring event, groundwater samples from select wells in the WIU and UIU (see CRA letter dated September 13, 1996 included in Appendix 12.2 for select wells) also will be analyzed for the SSIPL semi-VOC analytes. The SSIPL and groundwater monitoring schedule will be re-evaluated following the November 1999 monitoring event. The SSIPL analytes are presented in Table 12.3.

12.1.4 Parameters to be Tested and Frequency

Sample matrices, analytical parameters and frequencies of sample collection are presented in Table 12.1.

12.1.5 Data Quality Objectives (DQOs)

Data quality objectives (DQOs) are qualitative and quantitative statements which specify the quality of the data required to support decisions made during investigation activities and are based on the end uses of the data to be collected. As such, different data uses may require different levels of data quality. There are five analytical levels which address various data uses and the QA/QC effort and methods required to achieve the desired level of quality.

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
Groundwater Monitoring During Operation and Maintenance									
WTU, IU Groundwater (system startup to one year)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	44	5	5	3	57	3	171
WTU, IU Groundwater (Year 2 to Year 4)	water level pH SCOND temperature	SSIPL [4] VOC SSIPL Metals	44	5	5	3	57	2	114
WTU, IU Groundwater (November 1997)	water level pH SCOND temperature	SSIPL SVOC (Select Wells Only)	12	1	1	1	15	1	15
WTU, IU Groundwater (Year 6 to Termination)	water level pH SCOND temperature	SSIPL [5]	44	5	5	3	57	1	57
USU Groundwater (System startup to one year)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	5	1	1	1	8	2	16

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
USU Groundwater (Year 2 to Year 4)	water level pH SCOND temperature	SSIPL VOC SSIPL Metals	5	1	1	1	8	1	8
USU Groundwater (Year 6 and every 2nd year to termination)	water level pH SCOND temperature	SSIPL [5]	5	1	1	1	8	once every 2 years	8 every 2 years
All Monitoring Wells Groundwater (Year 5 and every 5th year to termination)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	once every 5 years	62 every 5 years
Residential Well Groundwater (system startup to one year)	pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	3	1	1	1	6	2	12
Residential Well Groundwater (Year 2 and every 2nd year until one year after confirmation)	pH SCOND temperature	SSIPL VOC SSIPL SVOC SSIPL Metals	3	1	1	1	6	once every 2 years	6 every 2 years

TABLE 12.1

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SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
Sediment (at confluence of south and east drainage ditches)		TCL VOC TCL SVOC TCL Pesticides/PCB	1	0	1	1	3	1	3
Surface Water (at confluence of south and east drainage ditches)	pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB	1	1	1	1	4	1	4
<u>Treatment System Monitoring</u>									
Treatment Plant Effluent Water (Month 1)	Influent/Effluent Flow	OEPA VOC [6] OEPA BNA OEPA Metals	1	0	0	0	1	8	8
Treatment Plant Effluent Water (Months 2 to termination)	Influent/Effluent Flow	OEPA VOC OEPA BNA OEPA Metals	1	0	0	0	1	12	12
Treatment Plant Air Emissions (Startup to termination)	Influent/Effluent Flow	PPL [7] VOC/ TO-14 [8]	2	0	0	0	2	1	2

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
Termination Monitoring [9]									
All Monitoring Wells Groundwater (one year prior to termination)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	4	248
All Monitoring Wells Groundwater (monthly for the first three months once cleanup standards are achieved)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	3	186
All Monitoring Wells Groundwater (Years 1 and 2 post-termination of extraction system)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	2	124

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
All Monitoring Wells Groundwater (Year 3 through 5 post-termination of extraction system)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	1	62
<u>Treatment System Sludge</u>									
Sludge		TCLP	TBD [10]	0	0	0	TBD	TBD	TBD

1 One trip blank sample will be shipped with each cooler of monitoring well samples collected for VOC analysis.
2 SCOND = Specific conductance
3 Matrix spike/matrix spike duplicate (MS/MSD) analyses are required for organic analyses. Samples designated for MS/MSD analyses will be collected at a frequency of one per group of twenty (20) or fewer investigative samples. For MS/MSD samples within a water matrix, triple the normal sample volumes will be collected for VOC, and double the normal volumes will be collected for extractable organics and PCB/pesticides. Inorganics analysis will require either MS/MSD or MS and a duplicate sample analysis.
4 A Site-Specific Indicator Parameter List (SSIPL) was confirmed in correspondence dated September 13 1996 and approved by USEPA and OEPA. The SSIPL analytes are presented in Table 12.3. The specific monitoring requirements for the WTU, IU and USU monitoring wells and residential wells are summarized in the September 13, 1996 correspondence which is reproduced in Appendix 12.2.
5 The SSIPL will be re-evaluated and submitted to USEPA and OEPA for modification and/or approval prior to the Year 6 monitoring event.
6 OEPA = Ohio Environmental Protection Agency Final effluent monitoring requirements.
7 PPL = Priority pollutant list of analytes.
8 TO-14 = "The determination of volatile organic compounds (VOCs) in Ambient Air Using Summa Passivated Canister Sampling and Gas Chromatographic Analysis", USEPA Compendium Method TO-14.
9 Frequency of sampling may change based on the results of monitoring as specified in the Consent Decree.
10 To be determined (TBD) based on sludge removal requirements of the treatment system.

DQOs have been established in accordance with the USEPA guidance document entitled "Data Quality Objectives for Remedial Response Activities - Development Process", dated March 1987, in conjunction with the document, "Data Quality Objectives for Remedial Response Activities - Example Scenario RI/FS Activities at a Site with Contaminated Soils and Groundwater", dated March 1987. Reference to these documents ensures that the database developed during the Site activities meets the objectives and quality necessary for its intended use.

DQOs can be classified for the measurement data by defining the level of analytical support assigned to each type of data measurement.

The following defines the different levels of analytical support:

i) Level I - Field screening or analysis using portable instruments;
ii) Level II - Field analyses using more sophisticated portable analytical instruments;
iii) Level III - All analyses performed in off-Site analytical laboratories using EPA procedures other than the Contract Laboratory Program (CLP) Routine Analytical Services (RAS);
iv) Level IV - CLP-RAS performed in a CLP analytical laboratory using CLP procedures; and
v) Level V - Non-standard analytical methods performed in an off-Site laboratory.

Table 12.2 presents the level of analytical support for each group of parameters.

TABLE 12.2

LEVELS OF DATA QUALITY OBJECTIVES (DQO) ANALYTICAL SUPPORT
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Matrix	*Analysis*	*Analytical Support*
Sediment	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCBs	Level III
Surface Water	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCBs	Level III
Groundwater (Quality Monitoring)	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCBs	Level III
	TAL Inorganics	Level III
	Water Level	Level I
	pH	Level I
	Specific Conductance	Level I
Groundwater (Residential Wells)	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCBs	Level III
	TAL Inorganics	Level V
Effluent Water (Treatment System)	OEPA VOCs	Level III
	OEPA BNAs	Level III
	OPEA Metals	Level III
Air (Treatment System Emissions)	Priority Pollutant Volatile Organic Compounds	Level III
Treatment Plant Sludge	Hazardous Waste Characteristics	Level III

12.1.6 Monitoring Schedule

The monitoring schedule is presented on Figure 8.1 of the O&M Plan.

12.2 PROJECT ORGANIZATION AND RESPONSIBILITY

The organization for the key staff with QA/QC responsibilities is presented in Figure 12.1.

A summary of responsibilities of key personnel follows:

Gary Gifford - Trust Chairperson - SNFT (Summit National Facility Trust)

- general overview of the project to ensure that the PRPs objectives are met
- participation in key negotiations with the USEPA
- liaison with USEPA and OEPA
- managerial guidance to the Engineering Consultant's Project Manager
- approval of the QAPP

Jack Michels - Project Manager - CRA

- technical guidance to SNFT
- participation in key technical negotiations with USEPA and SNFT
- liaison with USEPA and OEPA
- approval of the QAPP

Steven Day - QA/QC Officer - Analytical and Field Activities - CRA

- systems audits - laboratory activities
- overview and review field QA/QC
- coordinate supply of performance evaluation samples
- review laboratory QA/QC
- data validation and assessment
- advise on data corrective action procedures
- preparation and review of RD activities reports
- QA/QC representation of project activities
- management of field activities and field QA/QC
- data assessment
- preparation and review of RD activities report
- technical representation of field activities
- preparation of standard operating procedures (SOPs) for field activities
- approval of the QAPP

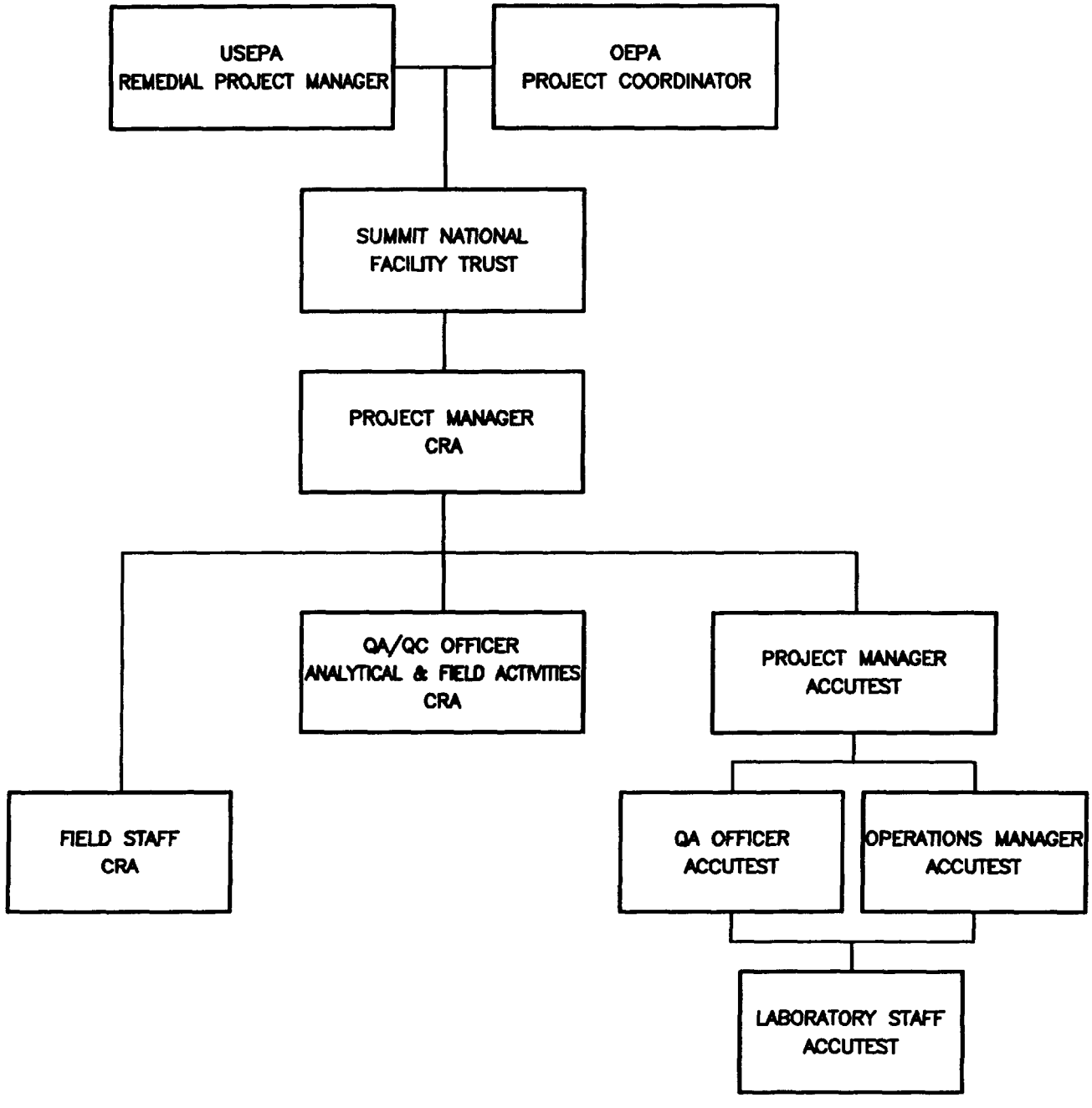

figure 12.1

QA/QC ORGANIZATION
SUMMIT NATIONAL SUPERFUND SITE
Deerfield Township Of Portage County, Ohio

CRA

Accutest
2235 Route 130
Dayton, New Jersey 08810
(908) 329-0200

- as analytical subcontractor to the Summit National Facility Trust (SNFT), will perform the majority of the chemical analyses of samples collected during the activities.

Patty Grieco - Project Manager - Accutest

- ensures all resources of the laboratory are available on an as-required basis
- overview of final analytical reports
- approval of the QAPP

William Sherding - Laboratory Director - Accutest

- coordinate laboratory analyses
- supervise in-house chain-of-custody
- schedule sample analyses
- oversee data review
- oversee preparation of analytical reports
- approve final analytical reports prior to submission to the Engineering Consultant

Maria Ruschke - QA Officer - Accutest

- overview laboratory quality assurance
- overview QA/QC documentation
- conduct detailed data review
- decide laboratory corrective actions, if required
- technical representation of laboratory QA procedures
- preparation of laboratory SOPs
- approval of the QAPP

Ron Van Blarcom - Sample Custodian - Accutest

- receive and inspect the incoming sample containers
- record the condition of the incoming sample containers
- sign appropriate documents
- verify chain of custody and its correctness
- notify Project manager of sample receipt and inspection
- assign a unique identification number and customer number and enter each into the sample receiving log
- with the help of the operations manager, initiate transfer of the samples to appropriate lab sections
- control and monitor access/storage of samples and extracts

Primary responsibility for project quality rests with CRA's QA/QC Officer - Analytical and Field Activities. Ultimate responsibility for project quality rests with CRA's Project Manager. Independent quality assurance will be provided by the Laboratory Project Manager and QA Officer prior to release of all data to the contractor.

USEPA RESPONSIBILITIES

The USEPA Region V Remedial Project Manager (RPM) will be responsible for the overview of this project. The RPM will also be responsible for providing approval of the QAPP. Anthony Rutter is the RPM for the Remedial Action activities. The USEPA Region V Quality Assurance Reviewer is responsible for reviewing and for providing final approval of the QAPP. In addition, external system and performance audits will be responsibility of USEPA.

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL AND SSIPL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

		Targeted Quantitation Limits [1]	
		Water (µg/L)	*Low Soil/Sediment (µg/kg)*
	Volatile Organic Compounds		
*	acetone	50	50
	benzene	5	5
	bromodichloromethane	5	5
	bromoform	5	5
	bromomethane	10	10
*	2-butanone	50	50
	carbon disulfide	5	5
	carbon tetrachloride	5	5
	chlorobenzene	5	5
	chloroethane	10	10
	chloroform	5	5
	chloromethane	10	10
	cis-1,3-dichloropropene	5	5
	dibromochloromethane	5	5
*	1,1-dichloroethane	5	5
*	1,2-dichloroethane	5	5
	1,1-dichloroethene	5	5
*	1,2-dichloroethene (total)	5	5
	1,2-dichloropropane	5	5
*	ethylbenzene	5	5
	2-hexanone	50	50
	methylene chloride	5	5
	4-methyl-2-pentanone	50	50
	styrene	5	5
	1,1,2,2-tetrachloroethane	10	10
	tetrachloroethene	5	5
*	toluene	5	5
	trans-1,3-dichloropropene	5	5
	1,1,1-trichloroethane	5	5
	1,1,2-trichloroethane	5	5
*	trichloroethene	5	5
	vinyl chloride	10	10
*	xylenes (total)	5	5

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL AND SSIPL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits	
	Water (µg/L)	*Low Soil/Sediment (µg/kg)*
Semi-Volatile Organic Compounds		
acenaphthene	10	330
acenaphthylene	10	330
anthracene	10	330
benzo(a)anthracene	10	330
benzo(a)pyrene	10	330
benzo(b)fluoranthene	10	330
benzo(g,h,i)perylene	10	330
benzo(k)fluoranthene	10	330
bis(2-chloroethoxy)methane	10	330
bis(2-chloroethyl)ether	10	330
2,2'-oxybis(1-chloropropane)	10	330
bis(2-ethylhexyl)phthalate	10	330
butylbenzylphthalate	10	330
4-bromophenylphenyl ether	10	330
carbazole	10	330
4-chloroaniline	10	330
2-chloronaphthalene	10	330
4-chlorophenyl phenyl ether	10	330
chrysene	10	330
dibenz(a,h)anthracene	10	330
dibenzofuran	10	330
1,2-dichlorobenzene	10	330
1,3-dichlorobenzene	10	330
1,4-dichlorobenzene	10	330
3,3'-dichlorobenzidine	50	660
diethylphthalate	10	330
dimethylphthalate	10	330
di-n-butyphthalate	10	330
di-n-octylphthalate	10	330
2,4-dinitrotoluene	10	330
2,6-dinitrotoluene	10	330
fluoranthene	10	330
fluorene	10	330
hexachlorobenzene	10	330
hexachlorobutadiene	10	330
hexachlorocyclopentadiene	10	330
hexachloroethane	10	330
indeno(1,2,3-cd)pyrene	10	330
* isophorone	10	330
2-methylnaphthalene	10	330

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL AND SSIPL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

		Targeted Quantitation Limits	
		Water (µg/L)	*Low Soil/Sediment (µg/kg)*
	Semi-Volatile Organic Compounds (Con't)		
	naphthalene	10	330
	2-nitroaniline	50	1,600
	3-nitroaniline	50	1,600
	4-nitroaniline	50	1,600
	nitrobenzene	10	330
	N-nitroso-di-n-propylamine	10	330
	N-nitrosodiphenylamine (diphenylamine)	10	330
	phenanthrene	10	330
	pyrene	10	330
	1,2,4-trichlorobenzene	10	330
	4-chloro-3-methylphenol	10	330
	2-chlorophenol	10	330
	2,4-dichorophenol	10	330
*	2,4-dimethylphenol	10	330
	2,4-dinitrophenol	50	1,600
	4,6-dinitro-2-methylphenol	50	1,600
*	2-methylphenol	10	330
*	4-methylphenol	10	330
	2-nitrophenol	10	330
	4-nitrophenol	50	1,600
	pentachlorophenol	50	1,600
*	phenol	10	330
	2,4,5-trichlorophenol	50	1,700
	2,4,6-trichlorophenol	10	330

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL AND SSIPL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits	
	Water (µg/L)	*Low Soil/Sediment (µg/kg)*
Pesticides		
aldrin	0.05	8
alpha-BHC	0.05	8
beta-BHC	0.05	8
alpha-chlordane	0.5	8
gamma-chlordane	0.5	8
4,4'-DDD	0.1	16
4,4'-DDE	0.1	16
4,4'-DDT	0.1	16
delta-BHC	0.05	16
dieldrin	0.1	16
endosulfan I	0.05	8
endosulfan II	0.1	16
endosulfan sulfate	0.1	16
endrin	0.1	16
endrin ketone	0.1	16
gamma-BHC (Lindane)	0.05	8
heptachlor	0.05	8
heptachlor epoxide	0.05	8
methoxychlor	0.5	8
toxaphene	1.0	160
PCBs		
Aroclor 1016	0.5	80
Aroclor 1221	0.5	80
Aroclor 1232	0.5	80
Aroclor 1242	0.5	80
Aroclor 1248	0.5	80
Aroclor 1254	1.0	160
Aroclor 1260	1.0	160

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL AND SSIPL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

		Targeted Quantitation Limits	
		Water (µg/L)	*Low Soil/Sediment (mg/kg)*
	Inorganics		
	aluminum	200	40
	antimony	60	12
	arsenic	10	2
	barium	200	40
	beryllium	5	1
*	cadmium	5	1
	calcium	5,000	1,000
	chromium	10	2
	cobalt	50	10
	copper	25	5
	iron	100	20
*	lead	3	0.6
	magnesium	5,000	1,000
	manganese	15	3
	mercury	0.2	0.1
*	nickel	40	8
	potassium	5,000	1,000
	selenium	5	1
	silver	10	2
	sodium	5,000	1,000
	thallium	10	2
	vanadium	50	10
	zinc	20	4
	cyanide	10	1

[1] Actual sample quantitation limits are highly matrix and laboratory dependant and are not always achievable. Targeted quantitation limits presented are for guidance only and may not be achievable.

* - Indicates a Site-specific Indicator Parameter List (SSIPL) analyte in accordance with CRA's letter dated September 13, 1996 to USEPA and OEPA. SSIPL to be revised based on results of November 1999 sampling event.

TABLE 12.4

TARGETED QUANTITATION LIMITS FOR TREATED GROUNDWATER EFFLUENT ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	*OEPA Discharge Limits* [2]
	Water (µg/L)	*Water* (µg/L)
Volatile Organic Compounds		
acetone	10	927
benzene	5	7
1,1-dichloroethane	5	7
1,2-dichloroethane	5	21
1,1-dichloroethene	5	5
1,2-dichloroethene (total)	5	26
ethylbenzene	5	5
methylene chloride	5	5
methyl ethyl ketone (2-butanone)	10	442
methyl isobutyl ketone (4-methyl-2-pentanone)	10	15
toluene	5	5
1,1,1-trichloroethane	5	12
trichloroethene	5	5
xylenes (total)	5	6
Base/Neutral Compounds		
bis(2-ethylhexyl)phthalate	10	10
isophorone	10	10
2-methylnapthalene	10	10
naphthalene	10	10
Acid Compounds		
4-chloro-3-methylphenol (p-chloro-m-cresol)	10	10
phenol	10	10
2-methylphenol	10	10
4-methylphenol	10	10

TABLE 12.4

TARGETED QUANTITATION LIMITS FOR TREATED GROUNDWATER EFFLUENT ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	*OEPA Discharge Limits* [2]
	Water (µg/L)	*Water* (µg/L)
Metals		
antimony	5	5
arsenic	5	7
iron	100	300
aluminum	200	536
barium	200	219
calcium	5,000	201,785
chromium (total)	5	5
cobalt	10	14
copper [3]	1.1	2
lead [3]	1	1
magnesium (dissolved)	5,000	72,151
manganese	15	6,818
nickel (dissolved)	10	14
potassium	5,000	6,415
zinc	20	188

1 Actual sample quantitation limits are highly matrix and laboratory dependant and are not always achievable. Targeted quantitation limits presented are for guidance only and may not be achievable.

2 Based on the OEPA Substantive Permit dated May 18, 1994 and revised inorganic discharge limits confirmed by CRA in letter dated November 29, 1994.

3 Targeted quantitation limit is the instrument detection limit.

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water (µg/L)
Volatile Organic Compounds	
acetone	5
benzene	1
bromodichloromethane	1
bromoform	1
bromomethane	1
2-butanone	5
carbon disulfide	1
carbon tetrachloride	1
chlorobenzene	1
chloroethane	1
chloroform	1
chloromethane	1
cis-1,3-dichloropropene	1
dibromochloromethane	1
1,1-dichloroethane	1
1,2-dichloroethane	1
1,1-dichloroethene	1
1,2-dichloroethene (total)	1
1,2-dichloropropane	1
ethylbenzene	1
2-hexanone	5
methylene chloride	2
4-methyl-2-pentanone	5
styrene	1
1,1,2,2-tetrachloroethane	1
tetrachloroethene	1
toluene	1
trans-1,3-dichloropropene	1
1,1,1-trichloroethane	1
1,1,2-trichloroethane	1
trichloroethene	1
vinyl chloride	1
xylenes (total)	1

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water ($\mu g/L$)
Semi-Volatile Organic Compounds	
acenaphthene	5
acenaphthylene	5
anthracene	5
benzo(a)anthracene	5
benzo(a)pyrene	5
benzo(b)fluoranthene	5
benzo(g,h,i)perylene	5
benzo(k)fluoranthene	5
benzyl alcohol	50
bis(2-chloroethoxy)methane	5
2,2'-oxybis(1-chloropropane)	5
bis(2-chloroisopropyl)ether	5
bis(2-ethylhexyl)phthalate	5
butyl benzyl phthalate	5
4-bromophenylphenyl ether	5
4-chloroaniline	5
2-chloronaphthalene	5
4-chlorophenyl phenyl ether	5
chrysene	5
dibenz(a,h)anthracene	5
dibenzofuran	5
1,2-dichlorobenzene	5
1,3-dichlorobenzene	5
1,4-dichlorobenzene	5
3,3'-dichlorobenzidine	20
diethylphthalate	5
dimethylphthalate	20
di-n-butyphthalate	5
di-n-octylphthalate	5
2,4-dinitrotoluene	5
2,6-dinitrotoluene	5
fluoranthene	5
fluorene	5
hexachlorobenzene	5
hexachlorobutadiene	5

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water (µg/L)
Semi-Volatile Organic Compounds (continued)	
hexachlorocyclopentadiene	5
hexachloroethane	5
indeno(1,2,3-cd)pyrene	5
isophorone	5
2-methylnaphthalene	5
naphthalene	5
2-nitroaniline	20
3-nitroaniline	20
4-nitroaniline	20
nitrobenzene	5
N-nitroso-di-n-propylamine	5
N-nitrosodiphenylamine (diphenylamine)	5
phenanthrene	5
pyrene	5
1,2,4-trichlorobenzene	5
benzoic acid	50
4-chloro-3-methylphenol	5
2-chlorophenol	5
2,4-dichorophenol	5
2,4-dimethylphenol	5
2,4-dinitrophenol	20
4,6-dinitro-2-methylphenol	20
2-methylphenol	5
4-methylphenol	5
2-nitrophenol	5
4-nitrophenol	20
pentachlorophenol	20
phenol	5
2,4,5-trichlorophenol	20
2,4,6-trichlorophenol	5

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water (µg/L)
Pesticides	
aldrin	0.01
alpha-BHC	0.01
beta-BHC	0.01
alpha-chlordane	0.01
gamma-chlordane	0.01
4,4'-DDD	0.01
4,4'-DDE	0.02
4,4'-DDT	0.02
delta-BHC	0.01
dieldrin	0.02
endosulfan I	0.01
endosulfan II	0.02
endosulfan sulfate	0.02
endrin	0.02
endrin ketone	0.02
gamma-BHC (Lindane)	0.01
heptachlor	0.01
heptachlor epoxide	0.01
methoxychlor	0.1
toxaphene	1.0
PCBs	
Aroclor 1016	0.20
Aroclor 1232	0.40
Aroclor 1242	0.20
Aroclor 1248	0.20
Aroclor 1254	0.20
Aroclor 1260	0.20

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water (µg/L)
Inorganics	
Aluminum	200
Antimony	5
Arsenic	5
Barium	200
Beryllium	5
Cadmium	4
Calcium	5,000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	3
Magnesium	5,000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5,000
Selenium	5
Silver	10
Sodium	5,000
Thallium	5
Vanadium	50
Zinc	20
Cyanide	10

1 Actual sample quantitation limits are highly matrix and laboratory dependant and are not always achievable. Targeted quantitation limits presented are for guidance only and may not be achievable.

TABLE 12.6

**TARGETED QUANTITATION LIMITS FOR
AIR AND TREATMENT SYSTEM SLUDGE ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO**

	Targeted Quantitation Limits [1]
	Air (ppbv) [2]
Air - Volatile Organic Compounds	
benzene	0.20
bromomethane	0.20
carbon tetrachloride	0.20
chlorobenzene	0.20
chloroethane	0.20
chloroform	0.20
chloromethane	0.20
1,3-dichloropropene	0.20
1,1-dichloroethane	0.20
1,2-dichloroethane	0.20
1,1-dichloroethene	0.20
1,2-dichloroethene	0.20
1,2-dichloropropane	0.20
ethylbenzene	0.20
methylene chloride	0.20
1,1,2,2-tetrachloroethane	0.20
tetrachloroethene	0.20
toluene	0.20
1,1,1-trichloroethane	0.20
1,1,2-trichloroethane	0.20
trichloroethene	0.20
vinyl chloride	0.20

TABLE 12.6

**TARGETED QUANTITATION LIMITS FOR
AIR AND TREATMENT SYSTEM SLUDGE ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO**

	Targeted Quantitation Limits [1] *TCLP Extract (mg/L)*
Treatment System Sludge Parameters	
TCLP Metals	
arsenic	0.50
barium	1.0
cadmium	0.0050
chromium	0.010
lead	0.50
mercury	0.0010
selenium	0.50
silver	0.010
TCLP Pesticides	
chlordane	0.0050
endrin	0.0010
Heptachlor	0.0010
heptachlor epoxide	0.0010
lindane	0.0010
methoxychlor	0.0050
toxaphene	0.050
TCLP Herbicides	
2,4-D	0.0040
2,4,5-TP (Silvex)	0.0040
TCLP Volatiles	
benzene	0.0040
carbon tetrachloride	0.0066
chlorobenzene	0.0067
chloroform	0.0094
1,2-dichloroethane	0.0083

TABLE 12.6

**TARGETED QUANTITATION LIMITS FOR
AIR AND TREATMENT SYSTEM SLUDGE ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO**

	Targeted Quantitation Limits [1] *TCLP Extract (mg/L)*
TCLP Volatiles (con't)	
1,1-dichloroethene	0.0097
methyl ethyl ketone	0.062
tetrachloroethene	0.0095
trichloroethene	0.0054
vinyl chloride	0.016
TCLP Semi-Volatiles	
o-cresol	0.017
m-cresol & p-cresol	0.024
1,4-dichlorobenzene	0.015
2,4-dinitrotoluene	0.0095
hexachlorobenzene	0.019
hexachloro-1,3-butadiene	0.015
hexachloroethane	0.019
nitrobenzene	0.013
pentachlorophenol	0.012
pyridine	0.10
2,4,5-trichlorophenol	0.015
2,4,6-trichlorophenol	0.010

[1] Actual sample quantitation limits are highly matrix and laboratory dependant and are not always achievable. Targeted quantitation limits presented are for guidance only and may not be achievable.

[2] ppbv = parts per billion by volume

12.4 SAMPLING PROCEDURES

The following subsections present the sampling procedures for the various media at the Site.

12.4.1 Equipment Cleaning

All sampling equipment which may come in contact with potentially contaminated materials shall be decontaminated prior to field use and after each sample is collected to prevent cross-contamination of the samples. Duplicate samples shall be collected concurrently with original samples, therefore, sampling equipment will not be decontaminated before collection of the duplicate. Decontamination of equipment will be performed as follows:

i) clean water and laboratory-grade detergent wash using a brush, if necessary, to remove all visible foreign matter;
ii) rinse thoroughly with potable water;
iii) rinse thoroughly with distilled or deionized water; and
v) allow the equipment to air dry on a clean aluminum foil as long as possible.

Following final rinse, openings will be visually inspected to verify they are free of soil particulates and other solid material which may contribute to possible sample cross-contamination.

Fluids used for cleaning will not be recycled. All wash water, rinse water and decontamination fluids will be treated in the on-Site treatment system.

12.4.2 Field Sampling

12.4.2.1 Sample Labeling

Each sample will be labeled with a unique sample number that will facilitate tracking and cross-referencing of sample information. The sample numbering system to be used is described as follows:

Example: GW-MMDDYY-XX-001

GW	- designates types of sample (GW-groundwater, SW-surface water, SD-sediment, SL-Sludge, RW-residential well, A-air)
MMDDYY	- designates date of collection presented as month/day/year
XX	- sampler's initials
001	- sequential number starting with 001 at the start of the project

Field QC samples will also be numbered with a unique sample number, consistent with the numbering system described above to prevent laboratory bias of field QC samples.

12.4.2.2 Field Log

The field logbook will be a bound document with consecutively numbered pages. The entries for each day will commence on a new page which will be dated. All entries will be made using waterproof ink. Corrections will be made by marking through the error with a single line, so as to remain legible, and initialing this action followed by writing the correction.

The following information will be recorded in the field logbook for each sample collected:

i) site location identification;
ii) unique sample identification number;
iii) date and time (in military time format) of sample collection;
iv) weather conditions;
v) designation as to the type of sample (groundwater, soil, etc.);
vi) designation as to the means of collection (grab, bailer, etc.);
vii) sample depth (where appropriate)
viii) name of sampler;
ix) analyses to be performed on sample;
x) volume and number of sample containers; and
xi) any other relevant comments such as odor, staining, texture, filtering, preservation, etc.

12.4.2.3 Chain-Of-Custody Forms

Chain-of-custody records will be used to track all samples from time of sampling to the arrival of samples at the laboratory.

Each sample container being shipped to the laboratory will contain a chain-of-custody form. The chain-of-custody form consists of four copies which are distributed to the sampler, to the shipper, to the contract laboratory and to the office file of CRA. The sampler and shipper will maintain their copies while the other two copies are enclosed in a waterproof enclosure within the shipping container. The laboratory, upon receiving the samples, will complete the remaining copies. The laboratory will maintain one copy for its records. The executed original will be returned to CRA with the data deliverables package. A typical chain-of-custody form is presented on Figure 12.2.

12.4.2.4 Sample Containers and Handling

Required sample containers, sample preservation methods, maximum holding times and filling instructions are provided in Table 12.7.

All samples will be placed in appropriate sample containers, labeled and properly sealed. The sample labels will include sample number, place of collection, date and time of collection and analyses to be performed. Samples will be cushioned within the shipping coolers by the use of vermiculite, foam chips and/or bubble pack. Samples will be kept cool by the use of sealed plastic bags of ice or cooler packs. A trip blank will accompany each shipment of multiple investigative groundwater samples submitted for VOC analysis.

Samples will be shipped by commercial courier or will be hand delivered on a daily basis to the project laboratory. The exception to this will be samples which are collected on a Sunday or holiday. For samples collected on a Sunday or holiday, additional ice will be placed in the coolers, the coolers will be sealed and kept in a designated secure area until they are picked up by the courier, or hand delivered to the laboratory, on the next business day.

Two seals comprised of chain-of-custody tape will be placed over the lid on the front right and back left of each shipping cooler prior to shipment to secure the lid and provide evidence that the samples have not been tampered with enroute to the laboratory.

Upon receipt of the cooler at the laboratory, the cooler will be inspected by the laboratory Sample Custodian. The condition of the cooler and seal will be noted on the chain-of-custody form by the Sample Custodian.

TABLE 12.7

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
MIAMI COUNTY INCINERATOR SITE
MIAMI COUNTY, OHIO

Analyses	*Sample Containers*	*Preservation* [1]	*Maximum Holding Time from Sample Collection* [2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
Groundwater/Residential Wells/Treatment System Samples						
SVOC, PCB Pesticides	Two 1-liter amber glass bottles per analysis	Iced	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottles	Overnight or Hand Deliver	Bubble Pack or Foam Chips
VOC	Three 40-mL teflon-lined septum vials	HCl to pH <2, Iced	14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner
Metals, Hardness	One 1-liter polyethylene bottle per analysis	HNO3 to pH <2,	6 months (mercury - 28 days) for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Total Cyanide	One 500-mL polyethylene or glass bottle	NaOH to pH>12, Iced	14 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
TSS, TDS, pH	One 1-liter polyethylene bottle	Iced	7 days for analysis (pH-immediately)	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Sediment						
SVOC, Pesticides/PCB	Two 4-ounce glass jars	Iced	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
VOC	Two 4-ounce glass jars	Iced	14 days for analysis	Fill completely	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Air						
VOC	One 6-L Summa® passivated stainless steel canister	None	14 days for analysis	6 liters	Overnight or Hand Deliver	Bubble Pack or Foam Chips

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
MIAMI COUNTY INCINERATOR SITE
MIAMI COUNTY, OHIO

Analyses	*Sample Containers*	*Preservation* [1]	*Maximum Holding Time from Sample Collection* [2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
Treatment Plant Sludge						
TCLP VOC	One 4-ounce jar	Iced	14 days for TCLP extraction 14 days after TCLP extraction for analysis	Fill completely	Overnight or Hand Deliver	Bubble Pack or Foam Chips
TCLP SVOC, Pesticides, Herbicides	One 8-ounce jar	Iced	14 days for TCLP extraction 7 days after TCLP extraction for preparative extraction 40 days after preparative extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble Pack or Foam Chips
TCLP Metals	One 8-ounce jar	Iced	180 days for TCLP extraction (mercury 28 days) 180 days from TCLP extraction for analysis (mercury 28 days)	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips

1 Samples will be shipped with bagged, cubed ice. Samples requiring refrigeration will be stored at 4°±2° following laboratory receipt and log-in.
2 These are technical holding times and are based on time elapsed from time of sample collection.

The Sample Custodian then will check the contents of the cooler with those samples listed on the chain-of-custody form. Any damage to the samples or discrepancies in sample identifications will be recorded in the remarks column of the chain-of-custody form and dated and signed. The Sample Custodian will inform the laboratory Project Manager of the problem who will contact CRA for resolution.

12.4.3 Sampling Protocols

12.4.3.1 Surface Water Sampling

Surface water samples will be collected in accordance with the following protocols:

1. New disposable gloves will be used when collecting each surface water sample. Additional new glove changes will be made as conditions warrant.

2. Samples will be collected by the grab sample method directly into precleaned sample containers. To obtain the sample, the sampler will approach the sample location from the downstream direction, invert the sample container prior to submergence (to avoid collecting debris floating on the surface) and then tilt the sample container in an upstream direction to permit the sample container to fill. To the extent possible, liquids will be collected a few inches below the surface and such that the collection container does not contact the sediment bed. When the container is full, it will be removed from the stream (in a manner that will ensure that no debris floating on the surface enters the sample container) and capped. Care will be taken to ensure that the cap interior is not handled.

3. Container preservation shipping and packaging requirements will be in accordance with Table 12.7.

12.4.3.2 Sediment Sampling

To the extent possible, sediment samples will be collected from locations underlying or immediately adjacent to the surface water sampling points. Sediment will be collected according to the following protocol:

1. Surface water samples of a particular location will be collected before sediment samples.

2. The sampling tool and all other instruments used in extracting the sediment samples will be precleaned between each sampling location using the prescribed decontamination procedure detailed in Section 12.4.1.

3. A new pair of disposable gloves will be used for each sample handled. Additional glove changes will be undertaken as conditions warrant.

4. Sediment samples will be collected with a spoon utensil manually scraping the upper two inches of the ditch bed.

5. Each sample (or portion thereof) collected will be placed directly in the appropriate sample container. Care will be taken to ensure that the cap interior is not handled.

6. Container, preservation, shipping and packing requirements will be in accordance with Table 12.7.

12.4.3.3 Groundwater Monitoring Well Sampling Protocols

Groundwater samples will be obtained using the sampling protocol which follows:

1. The depth of water in each well will be measured to the nearest 0.01 foot using an electric tape. The measuring device will be precleaned prior to use in each well using the cleaning sequence provided in Section 12.4.1.

2. Prior to sampling, each well will be purged using a precleaned, stainless steel bottom-filling bailer. Alternately, a stainless-steel outer casing submersible sampling pump or a Waterra foot valve with dedicated tubing may be used for well purging. The monitoring wells will be purged by removing a minimum of three standing well volumes of groundwater where the volume of standing water is calculated as follows:

$$V = 0.041\ d^2\ h$$

where:

V	=	volume of standing water in gallons
d	=	diameter of the well in inches
h	=	depth of water in feet

Field measurements of pH, conductivity and temperature of the evacuated water will be obtained and recorded following removal of each standing well volume and prior to sample collection. Well purging will continue until three consecutive and consistent readings (± 0.2 units for pH, ± five percent for conductivity and ± two degrees for temperature) of pH, conductivity and temperature are obtained or a maximum of five standing well volumes have been removed. In the event that a well is bailed dry prior to achieving three well volumes,

groundwater will be permitted to recover to a level sufficient for sample collection. The time that the well was bailed dry will be recorded and the well will be monitored for recovery. Upon recovery, the sample will be collected. All waste groundwater not collected for analysis will be disposed of in the on-Site treatment system.

3. Following well purging, samples will be collected using a pre-cleaned stainless-steel bailer attached to new polypropylene rope. If a submersible pump was used to purge the well, samples for inorganic parameters may be collected using the pump. However, all samples for organic analyses will be collected using a stainless-steel bailer. Sample containers will be filled with minimal agitation in order of decreasing analyte volatility, consistent with the requirements specified in Table 12.7.

4. Typically, unfiltered groundwater samples will be collected for inorganics analyses. The exception would be samples collected for dissolved metals analyses. These samples will be filtered in the field using a 2 µm pore size prefilter (if necessary) and a 0.45 µm pore size filter membrane.

5. A field duplicate sample will be collected at a frequency of one per ten investigative samples collected or at a minimum of one per sampling event. Sample containers will be filled in order of decreasing analyte volatility.

6. Samples will be collected for MS/MSD and MS/DUP analysis at a frequency of one per twenty investigative samples. The sample for MS/MSD and MS/DUP analysis will be collected from a well representative of the condition of the majority of the monitoring wells, turbid or non turbid. Samples will be collected from the representative monitoring wells using the same protocol as for the field duplicate with increased sample volume being collected for organics analyses.

The chain-of-custody forms sent to the project laboratory will indicate the samples collected for MS/MSD and MS/DUP analysis.

7. A field (rinsate) blank sample will be collected at a frequency of one per ten investigative samples collected or at a minimum of one per sampling event. This sample will consist of deionized water poured into, and then sampled out of, a precleaned bailer. This will provide a quality control check on the decontamination procedures employed for the bailers and sample containers.

12.4.3.4 Residential Well Sampling

The residential wells will be sampled according to the following protocol:

1. Water will be collected, if possible, from an outdoor spigot. The sampler should avoid taking the sample after flow through a water softener or home water treatment system.

2. Water will be allowed to run through the tap for fifteen minutes in order to purge the water system. Purged water will not be collected for disposal.

3. Samples will be collected as closely to the well heads as possible, and will be collected directly into sample containers in order of decreasing analyte volatility. VOCs will be collected first followed by SVOCs, pesticides/PCBs and inorganics. Samples from residential wells will not be filtered.

4. Three residential wells will be included in the monitoring program. The residential wells to be sampled will be selected by USEPA and Ohio EPA prior to each sampling round.

5. Container, preservation, shipping and packaging requirements will be in accordance with Table 12.7.

12.4.3.5 Treatment System Water

The influent and effluent waters will be sampled according to the following protocol:

1. Water will be collected from the appropriate sample tap.

2. Water will be allowed to run through the sample tap for one minute in order to purge the water system. Purged water will be collected and dispose of using the treatment system.

3. Samples will be collected directly into sample containers in order of decreasing analyte volatility.

4. Container, preservation, shipping and packaging requirements will be in accordance with Table 12.7.

12.4.3.6 Air Sampling

Samples of air emissions from the vapor phase carbon adsorber vents will be collected using the following protocol:

1. A short sampling probe will be inserted into the vent and attached to a pneumatic flow controlled pre-cleaned evacuated Summa® canister.

2. At the start of sampling, the canister valve will be opened to allow the emissions to flow into the canister. The pneumatic flow controller will

be calibrated to a flow rate of approximately 100 mL per minute for a one hour intergral sample of six liters.

3. Upon completion of sampling, the canister valve will be closed and the probe and controller removed.

4. The canister will be labeled and transported to the laboratory for analysis.

12.4.3.7 Treatment System Sludge Sampling

1. A new pair of disposable gloves will be used to collect the sample.

2. A sample from each of two Draimed storage bags will be randomly collected using stainless-steel tools and composited into a single sample.

3. Container, preservation, shipping and packaging requirements will be in accordance with Table 12.7.

12.7 ANALYTICAL PROCEDURES

The samples collected for chemical analyses will be analyzed using the methods listed in Table 12.8 and detailed in the respective SOPs included in Appendix 12.1. The rationale for selection of the parameters is based on the Statement of Work referenced in Section 12.1 and the September 13, 1996 correspondence regarding the SSIPL which is reproduced in Appendix 12.2.

TABLE 12.8

SUMMARY OF ANALYTICAL METHODS
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Matrix	*Parameter* [1]	*Method of Analysis* [2]
Sediment	TCL VOC	SOP for SW-846 8240
	TCL SVOC	SOP for SW-846 3550, 8270
	TCL PCB/Pesticides	SOP for SW-846 3550, 8080
Groundwater	SSIPL & TCL VOC	SOP for SW-846 8240
	SSIPL & TCL SVOC	SOP for SW-846 3520, 8270
	TCL PCB/Pesticides	SOP for SW-846 3520, 8080
	SSIPL & TAL Metals	SOP for SW-846 3010, 6010/7470
	Cyanide	SOP for SW-846 9010
Surface Water	TCL VOC	SOP for SW-846 8240
	TCL SVOC	SOP for SW-846 3520, 8270
	TCL PCB/Pesticides	SOP for SW-846 3520, 8080
Residential Water	TCL VOC	SOP for SW-846 8260
	TCL SVOC	SOP for SW-846 3520, 8270
	TCL PCB/Pesticides	SOP for SW-846 3520, 8080
	TAL Metals	SOP for SW-846 3010, 6010/7470
	Cyanide	SOP for SW-846 9010
Effluent Water	OEPA VOC	SOP for SW-846 8240
	OEPA BNA	SOP for SW-846 8270
	OEPA Metals	SOP for SW-846 3010, 6010/7470
	Iron, Calcium, Magnesium	SOP for SW-846 6010
	Total Dissolved Solids	SOP for EPA-WW 160.1
	Total Suspended Solids	SOP for EPA-WW 160.2
	Hardness, total	SOP for EPA-WW 130.1
	pH	SOP for EPA-WW 150.1
Air	PPL VOC	SOP for EPA-MCA 624/TO-14
Treatment Plant Sludge	TCLP Extraction	SOP for SW-846 1311
	TCLP VOC	SOP for SW-846 8240
	TCLP SVOC	SOP for SW-846 8270
	TCLP Pesticide	SOP for SW-846 8080
	TCLP Herbicide	SOP for SW-846 8150
	TCLP Metals	SOP for SW-846 3010,6010/7470

1 TCL = Target Compound List
VOC = Volatile Organic Compounds
SVOC = Semi-volatile Organic Compounds
PCB = Polychlorinated Biphenyls
OEPA = Ohio Environmental Protection Agency final effluent monitoring requirements
BNA = Base/Neutral and Acid Extractable Organic Compounds
PPL = Priority Pollutant List
SSIPL = Site-Specific Indicator Parameter List
TCLP = Toxicity Characteristic Leaching Procedure

2 Methods are referenced from:
SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods", EPA SW-846, 3rd edition with promulgated updates, November 1986.
EPA-MCA - "Methods for Organic Chemical Analysis of Industrial and Municipal Wastewater", 40 CFR Part 136, Appendix A.
TO-14 - "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Summa® Passivated Canister Sampling and Gas Chromatographic Analysis", USEPA Compendium Method TO-14.
EPA-WW- "Method for Chemical Analysis of Water and Wastes", EPA 600/4-79-020, revised March 1983.

12.9 DATA REDUCTION, VALIDATION AND REPORTING

The project laboratory will perform analytical data reduction and review in-house under the direction of the laboratory QA Officer. The laboratory QA Officer will be responsible for assessing data quality and advising of any data which were rated "preliminary" or "unacceptable" or other qualifications based on the established QC criteria. Data reduction, review and reporting by the laboratory is typically conducted as detailed in the following procedure.

1. Raw data produced and checked by the responsible analyst is turned over for independent review by another analyst.

2. The area supervisor reviews the data for attainment of quality control criteria established by the QAPP.

3. The area supervisor will decide whether any sample re-analysis is required.

4. Upon completion of all reviews and acceptance of the raw data by the supervisor, a report will be generated and sent to the Project Manager.

5. The Project Manager will complete a thorough inspection of all reports.

6. Upon acceptance of the preliminary reports by the Project Manager, final reports will be generated and signed by the laboratory Operations Manager or his designee.

7. A thorough review of a percentage of all data packages is performed by the laboratory Quality Assurance Officer or her designee.

Field data from direct-reading instruments (pH, conductance, temperature) will not require reduction. Laboratory data

reduction will be performed using the equations in the SOPs provided in Appendix 12.1.

CRA's QA/QC Officer - Analytical and Field Activities will conduct an evaluation of data reduction and reporting by the laboratory. These evaluations will consider the finished data sheets, field blank data and recovery data for surrogate and matrix spikes. The material will be checked for legibility, completeness, correctness and the presence of requisite dates, initials, and signatures. The results of these checks will be assessed and reported to CRA's Project Manager noting any discrepancies and their effect upon the acceptability of the data. All information garnered for QA/QC checks will be discussed in a QA/QC Validation report.

Validation of the analytical data will be performed by CRA's QA/QC Officer - Analytical and Field Activities based on the applicable evaluation criteria outlined in "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", EPA-540/R-94/013, February 1994 and "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review", EPA-540/R-94-012, February 1994. The assessment of analytical and field data will include checks for adherence to laboratory QA procedures and accuracy and precision criteria; and the presence of transmittal errors and anomalously high or low parameter values. The results of these data validations will be reported to the Project Manager, noting any problems and their effect upon the acceptability of the data.

Data produced from field measurements and sample collection activities that are used in the project reports will be appropriately identified and appended to the report. Where data have been reduced or summarized, the method of reduction will be documented in the report. In addition, field data will be audited for anomalously high or low values that may appear to be inconsistent with other data.

Laboratory data packages for chemical analyses will consist of the following deliverables:

i) a case narrative that includes a summary of analytical methods used and a description of any unusual action or conditions;

ii) dates of sample receipt, extraction/digestion and analysis;

iii) laboratory and field sample identification numbers;

iv) samples results in tabular format;

v) method blank sample summaries;

vi) surrogate compound recovery data and control limits;

vii) MS/MSD and MS/DUP recovery and RPD data and control limits;

viii) check sample data; and

ix) executed chain-of-custody forms.

The data packages will be stored with the evidentiary files as described in Section 12.5.4. The USEPA and OEPA, upon request, will receive (within 30 days of receipt) all raw data packages from the project laboratory.

APPENDIX 12.1

FIELD AND LABORATORY STANDARD OPERATING PROCEDURES

TEST NAME **DETERMINATION OF VOLATILE ORGANICS USING GC/MS SYSTEM**

METHOD REFERENCE SW-846 (METHOD 8240B) 3rd edition (Revision 2, September 1994)

1.0 SCOPE AND APPLICATION

1.1 The following method describes the analytical procedures which are utilized by Accutest to acquire samples for analysis of volatile organic compounds.

1.2 This analytical method is designed for nearly all types of samples, regardless of water content, including ground water, aqueous sludges, liquors, waste solvents, oily wastes, tars, filter cakes, sediments and soils.

1.3 Volatile water soluble compounds can be included in this analytical technique. However, for some low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4 The purgeable organics can be quantitated by Gas Chromatographic/Mass Spectrometric (GC/MS) following purge and trap utilizing the internal standard technique.

1.5 An additional method for sample introduction is direct injection. This technique has been tested for the analysis of waste oil diluted with hexacecane 1:1 (vol / vol) and may have application for the analysis of some alcohols and aldehyde in aqueous samples.

1.6 RDL (Reporting Detection Limit) is equivalent to the laboratory's Method Detection Limit (MDL). The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL will vary based on dilutions required to eliminate matrix interferences or weight and percent solids.

2.0 SUMMARY OF METHOD

2.1 This method is performed in accordance with EPA methodology 8240, from SW-846 (Revision 2, September 1994).

2.2 An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic (GC) column.

2.3 The volatile compounds are separated by the temperature programmed GC column and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.4 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.5 Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a 5 point curve.

2.6 Additional unknown peaks with a response > 10 % of the closest internal standard may be processed through a library search with comparison to a data base of approximately 54,000 spectra. An estimated concentration is quantitated by assuming a response factor of 1.

3.0 INTERFERENCES

3.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

3.2 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.4 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination.

4.0 SAMPLE HANDLING AND PRESERVATION AND HOLDING TIME

4.1 HANDLING and PRESERVATION

4.1.1 Container - 40 ml glass screw-cap VOA vial with Teflon-faced silicone septum.

4.1.2 The vials and septum should be washed and rinsed with distilled deionized water, then baked in oven at approximately 105^0 C for about one hour. Do not heat the septum for more than one hour, because the silicone begins to slowly degrade at 105^0 C. Precleaned vials may also be ordered.

4.1.3 When required, HCl is added to vial for aqueous samples as a preservative. Non-aqueous samples are never preserved.

4.1.4 Sample should be taken with care so as to prevent any air or bubbles entering vials creating headspace.

4.1.5 The samples must be protected from light and refrigerated at 4^0 C (+/-1) from the time of receipt until analysis.

4.2 HOLDING TIME

All samples are to be analyzed within 14 days of sampling (HCL preserved for aqueous sample) unless otherwise specified by the contract. If aqueous samples are received unpreserved, then analysis should occur within seven days of sampling.

5.0 APPARATUS AND MATERIALS

5.1 SYRINGE

5.1.1 10, 25, 50, 100, 500 and 5000 ul graduated syringes, manually held (Hamilton or equiv.).

5.1.2 5 ml glass gas tight syringes with Luerlok end, if applicable to the purging device.

5.2 BALANCE

5.2.1 Analytical balance capable of weighing 0.0001 gram.

5.2.2 Top-loading balance capable of weighing 0.1 g.

5.3 PURGE AND TRAP DEVICES

5.3.1 Two types of autosampler model are used for purging, trapping and desorbing the sample into GC column.

- Tekmar LSCII and ALS2016 and ALS2032.
- O.I.Model 4560 sample concentrator with 4551 vial multisampler.

5.3.2 The sample purger must be designed to accept 5 ml samples with a water column at least 3 cm deep.

5.3.3 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following absorbents (3-ring):

- 2,6-Diphenylene oxide polymer.
- Silica gel.
- Charcoal packing.

5.3.4 The trap should be conditioned overnight at 180^0 C by backflushing with an Helium gas flow at least 20 ml/min prior to use.

5.3.5 The desorber should be capable of rapidly heating the trap to 180^0 C for desorption.

5.4 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

5.4.1 Gas Chromatograph.

An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

5.4.2 Column.

75 m x 0.53mm ID capillary column coated with DB-624 (J&W Scientific), Rtx-502.2 (Restek), 3um film thickness or equivalent. Condition as per manufactures directions.

5.4.3 Mass Spectrometer.

Capable of scanning from 35-300 amu every 2 second or less utilizing a 70 volt (nominal) electron energy in the electron impact ionization mode.

Capable of producing a mass spectrum which meets all the criteria in Table 2 when injecting 50 ng of Bromofluorobenzene(BFB).

5.5 DATA SYSTEM

5.5.1 A computer system is interfaced to the mass spectrometer which allows the continuous acquisition and storage on machine readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

5.5.2 The computer utilizes software which allows searching any GC/MS data file for target analytes which display specific fragmentation patterns.

5.5.3 The AQUARIUS (HP-RTE A) and ENVIROQUANT (PC) data system is capable of quantitation using multipoint calibration and multipoint internal standards.

5.5.4 The recent version of the EPA/NBS mass spectral library (54,000 compounds) is being used for non target peak tentative identification.

5.5.5 Capable of producing an Extracted Ion Current Profile (EICP). The software can search a datafile for ions of a given mass and plot them versus time and/or scan number. Also able to integrate the ion abundances in an EICP between a specified time or scan number range.

5.5.6 Data can be archived to magnetic tape for long term storage.

6.0 REAGENTS AND STANDARDS

6.1 Solvent

Methanol: pesticide quality or equivalent. Store apart from other solvents.

6.2 Reagent water

6.2.1 Reagent water is defined as water in which an interferant is not observed at the method detection limit of the parameters of interest.

6.2.2 Reagent water is generated by either passing tap water through a bed of approximately one pound of activated carbon or by using the water purification system at Accutest which is a series of deionizers and carbon cartridges.

6.3 Stock standard solutions

6.3.1 Commercially prepared standards used.

6.3.1.1 Absolute (or equivalent): V8240 mixtures at 200 ug/ml concentration

6.3.1.2 Protocol (or equivalent) : the mix contains 2.0 mg/ml of the following in methanol

Bromomethane
Chloroethane
Chloromethane
Dichlorodifluoromethane
Trichlorofluoromethane
Vinyl Chloride

6.3.1.3 Acrolein/Acrylonitrile (10000 ug/ml)

Take 11.9 ul of a neat Acrolein and 11.5 ul of a neat Acrylonitrile standard and bring to 1 ml with methanol.

6.3.2 Stock standard solutions (except gases) must be replaced after 6 months or sooner if comparison with quality control check samples indicates a problem.

6.3.3 The purgeable gases standard should be replaced every two months or sooner if comparison with quality control check samples indicates a problem.

6.4 Internal Standard and Surrogate Solution.

Three internal standards (see Table 3) are used that exhibit similar analytical behavior to the compounds of interest.

Absolute (or equivalent): Internal standard mixture at 2000 ug/ml
surrogate mixture at 2000 ug/ml

6.5 Working standards

6.5.1 A 50 ug/ml working standard is utilized as the calibration, blank spike, and matrix spike solution.

6.5.2 All standard solutions (except gases) must be replaced after 2 months or sooner if comparison with quality control check samples indicates a problem (exceed 20% drift).

6.5.3 Prepare fresh gas standards weekly or sooner if comparison with quality control check samples indicates a problem(exceed 20% drift).

6.5.4 Refer to the Volatile Standards Logbook for preparation of working standards.

6.6 Bromofluorobenzene (BFB)

The BFB is prepared at 25 ug/ml by measuring 1 ul of Supelco Stock (25,000 ug/ml) and diluting in a crimp vial containing 1 ml of methanol.

7.0 CALIBRATION

7.1 The calibration range covered by the standards is 10, 20, 50, 100, 150, 200 ug/l.

7.1.1 Add 1 ul, 5 ul, 10 ul, 15 ul, and 20 ul of 50 ug/ml working standard individually into each 5 ml reagent water contained in gas tight syringe. Or

7.1.2 Add 10 ul, 20 ul, 50 ul, 100ul, 150 ul, and 200 ul of 50 ug/ml working standard individually into each 50 ml reagent water contained in volumetrics.

7.2 The linear range covered by this calibration is highest concentration standard.

7.3 Add 5 ul of internal standard and surrogate solution (see section 6.4) to each standard with a 10 ul syringe. This results in a concentration of 50 ug/L for each internal and surrogate standard.

7.4 Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 7.

7.5 The Response Factor (RF) is defined in section 10.1.

7.6 Initial calibration

The following criteria must be met for the initial calibration to be valid.

7.6.1 The percent relative standard deviation (% RSD) (see section 10.2) of calibration check compound (CCC) (see Table 5) must be less than 30 %.

7.6.2 The minimum average response factor (RF) of the system performance check compounds (SPCC) are listed in Table 5.

7.6.3 The %RSD should be less than 15% for the all other compounds. If the %RSD is >15%, the analyst must advise the team-leader or manager, the calibration may still be accepted. Other calibration options may be used for compounds falling outside 15%RSD such as a regression order that gives the least error.

7.7 Continuing calibration (CBCHK)

7.7.1 A continuing calibration check standard at mid-level concentration (50 ug/ml) must be acquired every 12 hrs.

7.7.2 The minimum RF of check standard for SPCC compound is shown on Table 5 .

7.7.3 The percent drift (% D, see section 10.3) for CCC must be less than 20.

7.7.4 If the CCCs are not required analytes by the permit, then all required analytes must meet the 20 %D.

7.7.5 If all of the above specified criteria are met, the continuing calibration is considered valid.

7.7.6 If either of the criteria fail, a new five point calibration must be performed.

7.7.7 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or retention time changes by more than 30 seconds from the last daily calibration check standard, the mass spectrometer must be inspected for malfunctions and corrections will be made, as appropriate.

8. PROCEDURE

8.1 Instrument conditions.

Recommended instrument conditions are listed in Table 1 Modifications are allowed as long as criteria of calibration are met.

8.2 Purge and Trap Device conditions.

See Table 1.

8.3 Daily GC/MS performance check.

8.3.1 Every 12 hours, inject 2 ul (50 ng) of BFB solution directly on column.

8.3.2 The GC/MS system must be checked to verify acceptable performance criteria are achieved (see Table 2)

8.3.3 This performance test must be passed before any samples, blanks or standards are analyzed.

8.3.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are met.

8.3.5 The injection time of the acceptable tune analysis, is considered the start of the 12 hour clock.

8.4 Daily calibration check

See section 7.7

8.5 Method blank (reagent water):

8.5.1 The acceptable method blank must be analyzed for every 12 hour time period or sooner.

8.5.2 Load 5 ml DI water with the 5 ml Luerlok syringe and add 5 ul of 50 ug/ml of internal standard and surrogate mixture to the syringe as a method blank. Analyze as per 8.6.

8.5.3 No compound can be present above the RDL (Reported Detection Limit). See Table 8.

8.5.4 Surrogates must meet Table 4 criteria.

8.5.5 If the method blank does not meet the surrogate criteria or if target analytes are detected above the RDL, the entire batch should be reanalyzed. See manager prior to further action.

8.6 Sample analysis

8.6.1 Rinse 5 ml syringes at least twice with organic-free water (reagent water).

8.6.2 Establish dilution of sample in order to fall within calibration range.

- from screen data.
- from acquired sample data.
- from history program.
- sample characteristics (appearance,odor)

8.6.3 Water samples.

Using Tekmar LSCII and ALS2016 and ALS2032 as purging system:

- pour the sample into the syringe until just overflowing.
- replace the syringe plunger and adjust the sample volume to 5 ml.
- care must be taken to prevent air into the syringe.

Using O.I.Model 4560 sample concentrator with 4551 vial multisampler

- place the 40 ml vial in the tray

8.6.4 Sediment/ soil samples.

Low-level soil method

- weigh approximately 5 g (or less) sample into disposable tared purge tube.
- attach purge tube to autosampler.
- add 5 ml reagent water into 5 ml syringe.

Medium-level soil method

The sample should be extracted/ or diluted in methanol, if less than 1.0 gram is to be used for analysis.

- weigh 4 g sample into VO vial containing 10 ml methanol and seal with Teflon lined septum.
- mix by hand shaking vigorously for 1 minute.
- let settle.
- aliquot proper amount of extract by using gas tight microsyringe.
- add an aliquot of the sample extract to a syringe containing 5 ml reagent water.

8.6.5 Add 5 ul of 50 ug/ml internal standard (I.S.) and surrogate mixture to syringe containing sample. The concentration of each I.S. and surrogate should be 50 ug/l without any dilution factors.

8.6.6 Attach the syringe to the valve on the TEKMAR ALS and inject into purge vial.

8.6.7 Purge the sample for 11 minutes with Helium.

8.6.8 Desorb the sample for 4 minutes by rapidly heating the trap to 180^0 C while backflushing with Helium.

8.6.9 Bake the trap for 12 minutes at 225^0 C to remove any residual purgeable compounds.

8.6.10 If the response for any ion exceeds the working range of the GC/MS system, dilute the sample or extract and re-analyze.

8.7 Data interpretation

8.7.1 Qualitative identification.

The targeted compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The criteria required for a positive identification are:

8.7.1.1 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criteria is the RRT of sample component must be within ± 0.06 RRT units of the standard.

8.7.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10 % (major abundant ion in the spectrum equals 100 %) should be present in the sample spectrum.

8.7.1.3 The relative intensities of these ion must agree within ± 30 % between the daily standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 20 and 80 %.

8.7.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficiently GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 % of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

8.7.2 Quantitative analysis

8.7.2.1 When a target compound has been identified, concentration (see section 10.4) will be based on the integrated area of the quantitation ion, normally the base peak (see Table 7).

8.7.2.2 If the sample produces an interference for the primary ion, use a secondary ion to quantitate (see Table 7). This is characterized by an excessive background

signal of the same ion which distorts the peak shape beyond a definitive integration. Also an interference could severely inhibit the response of the internal standard ion. This secondary ion must also be used to generate new calibration response factors.

8.8 Library search for tentatively identified compounds.
If a library search is requested, the analyst should perform a forward library search of NBS mass spectral library to tentatively identify 15 non-reported compounds.
Guidelines for making tentative identification are listed below.

8.8.1 These compounds should have a response greater than 10 % of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

8.8.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

8.8.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

8.8.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) should be present in the sample spectrum.

8.8.5 The relative intensities the major ions should agree within ± 20 %.

8.8.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

8.8.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

8.8.8 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

8.8.9 Quantitation will be performed on the nearest internal standard.

9. QUALITY CONTROL

QC Requirements Summary

BFB	Every 12 hrs.
Calibration Check std.	Every 12 hrs.
Batch blank	Every 12 hrs.
Matrix Spike	one per analytical batch.*
Matrix Spike Duplicate	one per analytical batch.*
Blank Spike (QCCS)	one per analytical batch.*
Surrogate	every sample and standard.
Internal Standard	every sample and standard.

* A batch is defined as a maximum of 20 samples, or an SDG, whichever is more frequent.

9.1 Daily GC/MS performance check - refer to section 8.3

9.2 Daily calibration check - refer to section 7.8

9.3 Method blank (reagent water) - refer to section 8.5

9.4 Matrix Spike(MS)/Matrix Spike Duplicate(MSD)/Blank spike(QCCS).

9.4.1 One sample is selected at random from each analytical batch of similar matrix types and spiked in duplicate with select compounds to check precision and reproducibility.

9.4.2 Blank spike (QCCS) is prepared to contain 20 ug/L each analyte in reagent water.

9.4.3 Matrix spikes are prepared by spiking an actual sample at a concentration of 50 ug/l or 50 ug/kg based on 5 g dry weight. This is prepared as outlined in 7.1.

9.4.4 Percent recoveries (% R) (see section 10.5) are compared to the acceptance criteria listed in Table 6.

Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 2SP.

9.4.5 A relative percent deviation (RPD) (see section 10.6) is calculated.

9.4.6 If matrix spikes do not meet criteria and the QC check sample (blank spike) does meet the criteria (see Table 6), matrix interference is to be assumed and the data is reportable.

9.5 Surrogate

9.5.1 All blanks, samples, and matrix spikes contain surrogate compounds which are used to monitor method performance.

9.5.2 If the recovery of any surrogate compound does not meet the control limits specified in Table 4 the recovery must be flagged and:

9.5.2.1 The calculation must be checked.

9.5.2.2 The sample must be reanalyzed if the recovery of any one surrogate is out of control limit.

9.5.4 Reanalysis is not required for samples exhibiting matrix interference, defined as excessive signal levels from target and non-target interfering peaks.

9.5.5 If surrogate recoveries are acceptable upon reanalysis, the data from the reanalysis is reported. If the reanalysis date did not meet the hold time, then both sets of data have to submitted with the reanalysis reported.

9.5.6 If surrogates are still outside control limits upon reanalysis, then both sets of data should be submitted with the first analysis reported.

9.6 Internal Standard.

9.6.1 Retention time for all internal standard must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 100 ug/l standard of initial calibration.

9.6.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area in the latest calibration standard (12 hr. time period).

9.6.3 If area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

9.6.4 If areas are acceptable upon reanalysis, the reanalysis data is reported.

9.6.5 If areas are unacceptable upon reanalysis, then both set of data are submitted with the original analysis reported.

10. CALCULATION

10.1 Response Factor (RF)

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

where: As = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cs = Concentration of the compound being measured (ug/l).
Cis = Concentration of the specific internal standard (ug/l).

10.2 Percent Relative Standard Deviation (% RSD)

$$\%RSD = \frac{SD}{RFav} \times 100$$

where: SD = Standard Deviation
RFav = Average response factor from initial calibration.

10.3 Percent Drift (%D).

$$\%D = \frac{(Cq - Cc)}{Cq} \times 100$$

where: Cq = Calibration Check Compound standard concentration.
Cc = Measured concentration using selected quantitation method.

10.4 Concentration (Conc.)

For water:

$$\text{Conc. (ug/l)} = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Vi}$$

For soil/sediment (on a dry weight basis):

$$\text{Conc. (ug/kg)} = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Ws \times M}$$

Where: Ac = Area of characteristic ion for compound being measured.
Vp = 5 ml (Total Purge Volume)
Vi = Initial volume of water purged (ml).
Ws = Weight of sample extracted (g).
M = (100 - % moisture in sample) / 100 or % solids / 100

10.5 Percent Recovery (% R)

$$\%\ R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

10.6 Relative Percent Difference (RPD)

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

Where: MSC = Matrix Spike Concentration
MSDC = Matrix Spike Duplicate Concentration

11.0 Documentation.

11.1 The Analytical Logbooks records the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

11.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in the comments section.

11.2 The Standards Preparation Logbook must be completed for all standard preparations. All information must be completed, the page must be signed and dated by the appropriate person.

11.2.1 The Accutest lot number must be cross referenced on the standard vial.

11.3 Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

12.0 Safety

The analyst should follow normal safety procedures as outlined in the Chemical Hygiene Plan.

Table 1

RECOMMENDED OPERATING CONDITION

Gas Chromatograph/ Mass Spectrometer

Carrier Gas(linear velocity)	Helium at 30 cm/sec
Mass range	35 - 260 amu
Electron Energy	70 volts (nominal)
Scan time	not to exceed 2 sec. per scan
Injection port temperature	200 - 225 C
Source temperature	200 - 250 C
Transfer line temperature	220 - 280 C
Analyzer temperature	220 - 250 C
Initial temperature	40 C
Time 1	3 minutes
Column temperature rate	8 degrees/min.
Final temperature	220 C
Total run time	35 - 50 mins

Purge and Trap Unit

Purge time	11 min.
Dry Purge	3 min
Desorb preheat	100 C
Desorb	4 min. at 180 C
Bake	12 min. at 225 C
Transfer line	100 - 130 C
Valve temperature	approx. transfer line temperature

Table 2

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15-40 of mass 95
75	30-60 of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5-9% of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Table 3

INTERNAL STANDARD IONS

Internal Standard	Prim/Sec. Ions
Bromochloromethane	128 / 49, 130, 51
1,4-Difluorobenzene	114 / 63,88
Chlorobenzene-d5	117 / 82, 119

Table 4

SURROGATE CONTROL LIMITS

Compound	(Prim/Sec. ions)	% Recovery (Water)	% Recovery (Soil)
1,2-Dichloroethane-d4	(65/102)	76 - 114	70 - 121
Toluene-d8	(98)	88 - 110	81 - 117
4-Bromofluorobenzene	(95 / 174, 176)	86 - 115	74 - 121

Table 5

Criteria for CCC and SPCC

Initial Calibration: Maximum % RSD for CCC is 30 %

Continuing Calibration: Maximum % D for CCC is 20 %

Minimum acceptable average relative response factor (RRF) for SPCC is shown :

Calibration check compounds (CCC)

Volatile
Vinyl chloride
1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

System Performance Check Compounds (SPCC)

Compound name	Minium RF
Chloromethane	0.3
1,1-Dichloroethane	0.3
Bromoform	>0.25
1,1,2,2-Tetrachloroethane	0.3
Chlorobenzene	0.3

Table 6

QC ACCEPTANCE CRITERIA*

Compound	Test Conc. (ug/l)	Limit for s (ug/l)	Range for X (ug/l)	Range p,ps (%)
Benzene	20	6.9	15.2-26.0	37-151
Bromodichloromethane	20	6.4	10.1-28.0	35-155
Bromoform	20	5.4	11.4-31.1	45-169
Bromomethane	20	17.9	D-41.2	D-242
Carbon tetrachloride	20	5.2	17.2-23.5	70-140
Chlorobenzene	20	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	20	25.9	D-50.4	D-305
Chloroform	20	6.1	13.7-24.2	51-138
Chloromethane	20	19.8	D-45.9	D-273
Dibromochloromethane	20	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	20	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	20	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	20	7.1	11.8-34.7	18-190
1,1-Dichloroeethane	20	5.1	14.2-28.4	59-155
1,2-Dichloroethane	20	6.0	14.3-27.4	49-155
1,1-Dichloroethene	20	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	20	5.7	13.6-28.4	54-156
1,2-Dichloropropane	20	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	20	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	20	10.4	7.6-32.4	17-183
Ethyl benzene	20	7.5	17.4-26.7	37-162
Methylene chloride	20	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	20	7.4	13.5-27.2	46-157
Tetrachloroethene	20	5.0	17.0-26.6	64-148
Toluene	20	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	20	4.6	13.7-30.1	52-162
1,1,2-Trichlorethane	20	5.5	14.3-27.1	52-150
Trichloroethene	20	6.6	18.5-27.6	71-157
Trichlorofluoromethane	20	10.0	8.9-31.5	17-181
Vinyl chloride	20	20.0	D-43.5	D-251

s = Standard deviation of four recovery measurements, in ug/L.
X = Average recovery for four recovery measurements, in ug/L.
p, ps = Percent recovery measured.
D = Detected; result must be greater than zero.
* Criteria from 40 CFR part 136 for Method 624.

Table 7

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

This table contains a more extensive list than the lab's routine analyte list.

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Acetone	58	43
Acetonitrile	41	41, 40, 39
Acrolein	56	55,58
Acrylonitrile	53	52, 51
Allyl alcohol	57	57, 58, 39
Allyl chloride	76	76, 41, 39, 78
Benzene	78	-
Benzyl chloride	91	91, 126, 65, 128
Bromoacetone	136	43, 136, 138, 93,95
Bromobenzene	156	77, 158
Bromochloromethane (I.S)	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43, 72
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Buytlbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64	66
2-Chlorethanol	49	49, 44, 43, 51, 80
bis-(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
Chloroprene	53	53, 88, 90, 51

Table 7 (cont'd)

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
3-Chloropropionitrile	54	54, 49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	75, 53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichlorethane	63	65, 63
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	79, 43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	55, 57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	88, 58, 43, 57
Epichlorohydrin	57	57, 49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	44, 43, 42
Ethyl methacrylate	69	69, 41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	44, 43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	43, 41, 42, 74

Table 7 (cont'd)

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malonitrile	66	66, 39, 65, 38
Methacrylonitrile	41	41, 67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	142, 127, 141
Methyl methacrylate	69	69, 41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	93, 66, 92, 78
Pentachloroethane	167	167, 130, 132, 165, 1
Propargyl alcohol	55	55, 39, 38, 53
6-Propiolactone	42	42, 43, 44
Propionitrile(ethyl cyanide)	54	54, 52, 55, 40
n-Propylamine	59	59, 41, 39

Table 7 (cont'd)

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
1,4-Difluorobenzene	114	63,88
Chlorobenzene-d_5	117	82,119
Bromochloromethane	128	49,130,51
4-Bromofluorobenzene	95	174, 176
1,2-Dichloroethane-d_4	65	102
Toluene-d_8	98	

Compound (1)	RDL (2)	RDL (2)
	Water	Soil*
Acetone	0.92	0.92
Acrolein	7.2	7.2
Acetonitrile	100	100
Acrylonitrile	6	6
Benzene	0.4	0.4
Bromodichloromethane	0.55	0.55
Bromoform	0.47	0.47
Bromomethane	1.2	1.2
2-Butanone	0.62	0.62
n-Butyl Alcohol	10	10
Butly Acetate	5	10
Carbon Disulfide	0.97	0.97
Carbon Tetrachloride	0.66	0.66
Chlorobenzene	0.67	0.67
Chloroethane	0.89	0.89
Chloroform	0.94	0.94
Chloromethane	1.0	1.0
2-Chloroethyl vinyl ether	1.0	1.0
Cyclohexanone	10.0	10.0
Cumene	5.0	5.0
1,2-Dibromoethane	5.0	5.0
Dichlorodifluoromethane	5.0	5.0
Dibromochloromethane	0.21	0.21
1,1-Dichloroethane	0.89	0.89
1,2-Dichloroethane	0.83	0.83
1,1-Dichloroethylene	0.97	0.97
1,2-Dichloroethene, total	0.92	NA
1,2-Dichlorobenzene	0.67	0.67
cis-1,2-Dichloroethylene	0.92	0.92
trans-1,2-Dichloroethylene	0.92	0.92
1,2-Dichloropropane	0.72	0.72
1,3-Dichlorobenzene	0.52	0.52
cis-1,3-dichloropropene	0.56	0.56
trans-1,3-dichloropropene	0.47	0.47
1,4-Dichlorobenzene	0.44	0.44
1,4-Dioxane	150	150
Di-Isopropyl Ether	0.88	0.88
Ethylene Dibromide		NA
Ethylbenzene	0.76	0.76
Epichlorohydrin	5	5
2-Ethoxyethanol	10	10
Ethyl Acetate	10	10
Ethyl Ether	10	10
Freon 113	5	NA
Hexane	5	NA
2-Hexanone	0.71	0.71
Heptane	5	NA
Methylene Chloride	0.64	0.64

Compound (1)	RDL (2) Water	RDL (2) Soil*
4-methyl-2-pentanone	1.3	1.3
MTBE	0.65	NA
1-Methylnaphthalene	5	NA
2-Methylnaphthalene	5	NA
Methylnaphthalene, total	5	NA
Dimethylnaphthalene, tota	5	NA
Dimethylnaphthalene	5	NA
Dimethyl Aniline	5	NA
Naphthalene	1	NA
2-Nitropropane	10	NA
Styrene	0.47	0.47
1,1,2,2-Tetrachloroethane	0.31	0.3
Tetrachloroethylene	0.95	0.95
Tetrahydrofuran	0.95	NA
Toluene	0.38	0.38
1,1,1-Trichloroethane	0.65	0.65
1,1,2-Trichloroethane	0.59	0.59
Trchlorofluoromethane	1.1	NA
Trichloroethylene	0.54	0.54
1,2,4-Trimethlybenzene	10	NA
1,3,5-Trimethlybenzene	10	NA
TBA	8.9	NA
Vinyl Acetate	0.59	0.59
Vinyl Chloride	1.6	1.6
m,p-xylene	1.0	1.0
p-xylene	1.0	NA
m-xylene	1.0	NA
o-xylene	1.0	1.0
Methyl methacrylate	5.0	NA
Ethylenimine	IND	IND

(*) - Wet weight basis; values will be higher upon calculation to dry weight.
RDL - Reported Detection Limit.
All values expressed in ppb.
(1) Compounds per method List Definition Report.
(2) Current RDL.
IND - Not purgable at any significant concentration.

Lab Manager: _____
QA Manager: _____

TEST NAME **DETERMINATION OF VOLATILE ORGANICS USING GC/MS SYSTEM**

METHOD REFERENCE SW-846 - 8260A (Revision 1, September 1994).

1.0 SCOPE AND APPLICATION

1.1 The following method describes the analytical procedures which are utilized by Accutest to acquire samples for analysis of volatile organic compounds.

1.2 This analytical method is designed for nearly all types of samples, regardless of water content, including ground water, aqueous sludges, liquors, waste solvents, oily wastes, tars, filter cakes, sediments and soils.

1.3 Volatile water soluble compounds can be included in this analytical technique. However, for some low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4 The purgeable organics can be quantitated by Gas Chromatographic/Mass Spectrometric (GC/MS) following purge and trap utilizing the internal standard technique.

1.5 An additional method for sample introduction is direct injection. This technique has been tested for the analysis of waste oil diluted with haxacecane 1:1 (vol / vol) and may have application for the analysis of some alcohols and aldehyde in aqueous samples.

1.6 RDL (Reporting Detection Limit) may vary depending on matrix interferences, sample volumes or weight and percent moisture. The Method Detection Limit (MDL) is defined as the minimum concentration of a subtance that can be measured and reported with 99% confidence that the value is above zero. The RDL is equivalent to the MDL.

2.0 SUMMARY OF METHOD

2.1 This method is performed in accordance with EPA methodology 8260, from SW-846 (Revision 1, September 1994).

2.2 An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic (GC) column.

2.3 The volatile compounds are separated by the temperature programmed GC column and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.4 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.5 Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a 5 point curve.

2.6 Additional unknown peaks with a response > 10 % of the closest internal standard may be processed through a library search with comparison to a data base of approximately 54,000 spectra. An estimated concentration is quantitated by assuming a response factor of 1.

3.0 INTERFERENCES

3.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

3.2 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.4 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination.

4.0 SAMPLE HANDLING AND PRESERVATION AND HOLDING TIME

4.1 HANDLING and PRESERVATION

4.1.1 Container - 40 ml glass screw-cap VOA vial with Teflon-faced silicone septum.

4.1.2 The vials and septum should be washed and rinsed with distilled deionized water, then baked in oven at 105^0 C for approximately one hour. Do not heat the septum for more than one hour, because the silicone begins to slowly degrade at 105^0 C.

4.1.3 When required, HCl is added to vial for aqueous samples as a preservative. Non-aqueous samples are never preserved.

4.1.4 Sample should be taken with care so as to prevent any air or bubbles entering vials creating headspace.

4.1.5 The samples must be protected from light and refrigerated at 4^0C (+/-!1from the time of receipt until analysis.

4.2 HOLDING TIME

All samples are to be analyzed within 14 days of sampling (HCL preserved for aqueous sample) unless otherwise specified by the contract. If aqueous samples are received unpreserved, then analysis should occur within seven days of sampling.

5.0 APPARATUS AND MATERIALS

5.1 SYRINGE

5.1.1 10, 25, 50, 100, 500 and 5000 ul graduated syringes, manually held (Hamilton or equiv.).

5.1.2 5 ml glass gas tight syringes with Luerlok end, if applicable to the purging device.

5.2 BALANCE

5.2.1 Analytical balance capable of weighing 0.0001 gram.

5.2.2 Top-loading balance capable of weighing 0.1 g.

5.3 PURGE AND TRAP DEVICES

5.3.1 Two types of autosampler model are used for purging, trapping and desorbing the sample into GC column.

- Tekmar LSCII and ALS2016 and ALS2032.
- O.I.Model 4560 sample concentrator with 4551 vial multisampler.

5.3.2 The sample purger must be designed to accept 5 ml samples with a water column at least 3 cm deep.

5.3.3 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following absorbents (3-ring):

- 2,6-Diphenylene oxide polymer.
- Silica gel.
- Charcoal packing.

5.3.4 The trap should be conditioned overnight at 180^0 C by backflushing with an Helium gas flow at least 20 ml/min prior to use.

5.3.5 The desorber should be capable of rapidly heating the trap to 180^0 C for desorption.

5.4 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

5.4.1 Gas Chromatograph.

An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

5.4.2 Column.

75 m x 0.53mm ID capillary column coated with DB-624 (J&W Scientific), Rtx-502.2 (Restek), 3um film thickness or equivalent. Condition as per manufactures directions.

5.4.3 Mass Spectrometer.

Capable of scanning from 35-300 amu every 2 second or less utilizing a 70 volt (nominal) electron energy in the electron impact ionization mode.

Capable of producing a mass spectrum which meets all the criteria in Table 2 when injecting 50 ng of Bromofluorobenzene(BFB).

5.5 DATA SYSTEM

5.5.1 A computer system is interfaced to the mass spectrometer which allows the continuous acquisition and storage on machine readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

5.5.2 The computer utilizes software which allows searching any GC/MS data file for target analytes which display specific fragmentation patterns.

5.5.3 The AQUARIUS (HP-RTE A) and ENVIROQUANT (PC) data system is capable of quantitation using multipoint calibration and multipoint internal standards.

5.5.4 The recent version of the EPA/NBS mass spectral library (54,000 compounds) is being used for non target peak tentative identification.

5.5.5 Capable of producing an Extracted Ion Current Profile (EICP). The software can search a datafile for ions of a given mass and plot them versus time and/or scan number. Also able to integrate the ion abundances in an EICP between a specified time or scan number range.

5.5.6 Data can be archived to magnetic tape for long term storage.

6.0 REAGENTS AND STANDARDS

6.1 Solvent

Methanol: pesticide quality or equivalent. Store apart from other solvents.

6.2 Reagent water

6.2.1 Reagent water is defined as water in which an interferant is not observed at the method detection limit of the parameters of interest.

6.2.2 Reagent water is generated by either passing tap water through a bed of approximately one pound of activated carbon or by using the water purification system at Accutest which is a series of deionizers and carbon cartridges.

6.3 Stock standard solutions

6.3.1 Commercially prepared standards used.

6.3.1.1 Absolute (or equivalent): V8260 mixtures (part # 33001) at 200 ug/ml concentration

6.3.1.2 Protocol (or equivalent). The mix contains 2.0 mg/ml of the following in methanol.

Bromomethane
Chloroethane
Chloromethane
Dichlorodifluoromethane
Trichlorofluoromethane
Vinyl Chloride

6.3.1.3 Acrolein/Acrylonitrile (10000 ug/ml)

Take 11.9 ul of a neat Acrolein and 11.5 ul of a neat Acrylonitrile standard and bring to 1 ml with methanol.

6.3.2 Stock standard solutions (except gases) must be replaced after 6 months or sooner if comparison with quality control check samples indicates a problem.

6.3.3 The purgeable gases standard should be replaced every two months or sooner if comparison with quality control check samples indicates a problem.

6.4 Internal Standard and Surrogate Solution.

Four internal standards (see Table 3) are used that exhibit similar analytical behavior to the compounds of interest.

Absolute (or equivalent): Internal standard mixture at 2000 ug/ml (part # 21002)
surrogate mixture at 2000 ug/ml (part # 20013)

6.5 Working standards

6.5.1 A 50 ug/ml working standard is utilized as the calibration, blank spike, and matrix spike solution.

6.5.2 All standard solutions (except gases) must be replaced after 2 months or sooner if comparison with quality control check samples indicates a problem (exceed 20% drift).

6.5.3 Prepare fresh gas standards weekly or sooner if comparison with quality control check samples indicates a problem(exceed 20% drift).

6.5.4 See the Volatiles Standard Logbook for preparation of working standard.

6.6 Bromofluorobenzene (BFB)

The BFB is prepared at 25 ug/ml by measuring 1 ul of Supelco Stock (25,000 ug/ml) and diluting in a crimp vial containing 1 ml of methanol.

7.0 CALIBRATION

7.1 The calibration range covered by the standards is 10, 20, 50, 100, 150, 200 ug/l.

7.1.1 Add 1 ul, 2 ul, 5 ul, 10 ul, 15 ul, and 20 ul of 50 ug/ml working standard individually into each 5 ml reagent water contained in gas tight syringe. Or

7.1.2 Add 10 ul, 20 ul, 50 ul, 100ul, 150 ul, and 200 ul of 50 ug/ml working standard individually into each 50 ml reagent water contained in volumetrics.

7.2 The linear range covered by this calibration is highest concentration standard.

7.3 Add 5 ul of internal standard and surrogate solution (see section 6.4) to each standard with a 10 ul syringe. This results in a concentration of 50 ug/L for each internal and surrogate standard.

7.4 Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 7.

7.5 The Response Factor (RF) is defined in section 10.1.

7.6 Initial calibration

The following criteria must be met for the initial calibration to be valid.

7.6.1 The percent relative standard deviation (% RSD) (see section 10.2) of calibration check compound (CCC) (see Table 5) must be less than 30 %.

7.6.2 The minimum average response factor (RF) of the system performance check compounds (SPCC) are listed in Table 5.

7.6.3 The %RSD should be less than 15% for the all other compounds. If the %RSD is >15%, the analyst must advise their team-leader or manager, the calibration may still be accepted. Other calibration options may be used for compounds falling outside 15%RSD, such as regression order.

7.7 Continuing calibration (CBCHK)

7.7.1 A continuing calibration check standard at mid-level concentration (50 ug/ml) must be acquired every 12 hrs.

7.7.2 The minimum RF of check standard for SPCC compound is shown on Table 5 .

7.7.3 The percent drift (% D, see section 10.3) for CCC must be less than 20.

7.7.4 If the CCCs are not required analytes by the permit, then all required analytes must meet the 20 %D.

7.7.5 If all of the above specified criteria are met, the continuing calibration is considered valid.

7.7.6 If either of the criteria fail, a new five point calibration must be performed.

7.7.7 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or retention time changes by more than 30 seconds from the last daily calibration check standard, the mass spectrometer must be inspected for malfunctions and corrections will be made, as appropriate.

8. PROCEDURE

8.1 Instrument conditions.

Recommended instrument conditions are listed in Table 1 Modifications are allowed as long as criteria of calibration are met.

8.2 Purge and Trap Device conditions.

See Table 1.

8.3 Daily GC/MS performance check.

8.3.1 Every 12 hours, inject 2 ul (50 ng) of BFB solution directly on column.

8.3.2 The GC/MS system must be checked to verify acceptable performance criteria are achieved (see Table 2)

8.3.3 This performance test must be passed before any samples, blanks or standards are analyzed.

8.3.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are met.

8.3.5 The injection time of the acceptable tune analysis, is considered the start of the 12 hour clock.

8.4 Daily calibration check

See section 7.7

8.5 Method blank (reagent water):

8.5.1 The acceptable method blank must be analyzed for every 12 hour time period or sooner.

8.5.2 Load 5 ml D.I. water with the 5 ml Luerlok syringe and add 5 ul of 50 ug/ml of internal standard and surrogate mixture to the syringe as a method blank. Analyze as per 8.6.

8.5.3 No compound can be present above the EQL (Estimated Quantitation Limits). See Table 8 for EQLs.

8.5.4 Surrogates must meet Table 4 criteria.

8.5.5 If the method blank does not meet surrogate criteria or contains target analytes above the PQL, the entire batch must be reanalyzed.

8.6 Sample analysis

8.6.1 Rinse 5 ml syringes at least twice with organic-free water (reagent water).

8.6.2 Establish dilution of sample in order to fall within calibration range.

- utilize screen data.
- utilize acquired sample data.
- utilize the history program.
- sample characteristics (appearance,odor)

8.6.3 Water samples.

Using Tekmar LSCII and ALS2016 and ALS2032 as purging system:

- pour the sample into the syringe until just overflowing.
- replace the syringe plunger and adjust the sample volume to 5 ml.
- care must be taken to prevent air into the syringe.

Using O.I.Model 4560 sample concentrator with 4551 vial multisampler

- place the 40 ml vial in the tray

8.6.4 Sediment/ soil sample

Low-level soil method

- weigh approximately 5 g (or less) sample into disposable tared purge tube.
- attach purge tube to autosampler.
- add 5 ml reagent water into 5 ml syringe.

Medium-level soil method

The sample should be extracted/ or diluted in methanol, if sample has to run less than 0.5 grams.

- weigh 4 g sample into VO vial containing 10 ml methanol and seal with teflon lined septum.
- mix by hand shaking vigorously for approximately 1 minute.
- let settle.
- aliquot proper amount of extract by using gas tight microsyringe.
- add an aliquot of the sample extract to a syringe containing 5 ml reagent water.

8.6.5 Add 5 ul of 50 ug/ml internal standard (I.S.) and surrogate mixture to syringe containing sample. The concentration of each I.S. and surrogate should be 50 ug/l without any dilution factors.

8.6.6 Attach the syringe to the valve on the TEKMAR ALS and inject into purge vial.

8.6.7 Purge the sample for 11 minutes with Helium.

8.6.8 Desorb the sample for 4 minutes by rapidly heating the trap to 180^0 C while backflushing with Helium.

8.6.9 Bake the trap for 12 minutes at 225^0 C to remove any residual purgeable compounds.

8.6.10 If the response for any ion exceeds the working range of the GC/MS system, dilute the sample or extract and re-analyze.

8.7 Data interpretation

8.7.1 Qualitative identification.

The targeted compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The criteria required for a positive identification are:

8.7.1.1 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criteria is the RRT of sample component must be within ± 0.06 RRT units of the standard.

8.7.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10 % (major abundant ion in the spectrum equals 100 %) should be present in the sample spectrum.

8.7.1.3 The relative intensities of these ion must agree within ± 30 % between the daily standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 20 and 80 %.

8.7.1.4 Structural isomers that produce very similar mass specrtra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficiently GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 % of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

8.7.2 Quantitative analysis

8.7.2.1 When a target compound has been identified, concentration (see section 10.4) will be based on the integrated area of the quantitation ion, normally the base peak (see Table 7).

8.7.2.2 If the sample produces an interference for the primary ion, use a secondary ion to quantitate (see Table 7). This is characterized by an excessive background signal of the same ion which distorts the peak shape beyond a definitive integration. Also an interference could severely inhibit the response of the internal standard ion. This secondary ion must also be used to generate new calibration response factors.

8.8 *Library search for tentatively identified compounds.*

If a library search is requested, the analyst should perform a forward library search of NBS mass spectral library to tentatively identify 15 non-reported compounds.

Guidelines for making tentative identification are listed below.

8.8.1 These compounds should have a response greater than 10 % of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

8.8.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

8.8.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

8.8.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) should be present in the sample spectrum.

8.8.5 The relative intensities the major ions should agree within ± 20 %.

8.8.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

8.8.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

8.8.8 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

8.8.9 Quantitation will be performed on the nearest internal standard.

9. QUALITY CONTROL

QC Requirements Summary

BFB	Every 12 hrs.
Calibration Check std.	Every 12 hrs.
Batch blank	Every 12 hrs.
Matrix Spike	one per analytical batch.*
Matrix Spike Duplicate	one per analytical batch.*
Blank Spike (QCCS)	one per analytical batch.*
Surrogate	every sample and standard.
Internal Standard	every sample and standard.

* A batch is defined as a maximum of 20 samples, or an SDG, whichever is more frequent.

9.1 Daily GC/MS performance check - refer to section 8.3

9.2 Daily calibration check - refer to section 7.8

9.3 Method blank (reagent water) - refer to section 8.5

9.4 Matrix Spike(MS)/Matrix Spike Duplicate(MSD)/Blank spike(QCCS).

9.4.1 One sample is selected at random from each analytical batch of similar matrix types and spiked in duplicate with select compounds to check precision and accuracy.

9.4.2 Blank spike (QCCS) is prepared to contain 20 ug/L each analyte in reagent water.

9.4.3 Matrix spikes are prepared by spiking an actual sample at a concentration of 50 ug/l or 50 ug/kg based on 5 g dry weight. This is prepared as outlined in 7.1.

9.4.4 Percent recoveries (% R) (see section 10.5) are compared to the acceptance criteria listed in Table 6.

Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 2SP.

9.4.5 A relative percent deviation (RPD) (see section 10.6) is calculated.

9.4.6 If matrix spikes do not meet criteria and the QC check sample (blank spike) does meet the criteria (see 9.4.7 , Table 6), matrix interference is assumed and the data is reportable.

9.4.7 The single laboratory accuracy and precision data (Table 6) was obtained for the method analytes from water. Compare x (average recovery) and s (standard deviation of the recovery) for each analyte to the Table 9. Results are comparable if the calculated standard deviation of the recovery does not exceed 2.6 times the RSD (Table 9) or 20%, which is greater, and the mean recovery lies within the interval x +/- 3s or x +/- 30%, whichever is greater.

9.5 Surrogate

9.5.1 All blanks, samples, and matrix spikes contain surrogate compounds which are used to monitor method performance.

9.5.2 If the recovery of any surrogate compound does not meet the control limits specified in Table 4, the result must be flagged and:

Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 3SP.

9.5.2.1 The calculation must be checked.

9.5.2.2 The sample must be reanalyzed if the recovery of any one surrogate is out of control limit.

9.5.4 Reanalysis is not required if the sample exhibits matrix interference, defined as excessive signal levels from target or non-target interfering peaks.

9.5.5 If surrogate recoveries are acceptable upon reanalysis, the data from the reanalysis is reported. If the reanalysis date did not meet the hold time, then both sets of data have to submitted with the reanalysis reported.

9.5.6 If surrogates are still outside control limits upon reanalysis, then both sets of data should be submitted with the first analysis reported.

9.6 Internal Standard.

9.6.1 Retention time for all internal standard must be within $\pm$ 30 seconds of the corresponding internal standard in the latest continuing calibration or 100 ug/l standard of initial calibration.

9.6.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area in the latest calibration standard (12 hr. time period).

9.6.3 If area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

9.6.4 If areas are acceptable upon reanalysis, the reanalysis data is reported.

9.6.5 If areas are unacceptable upon reanalysis, then both set of data are submitted with the original analysis reported.

10. CALCULATION

10.1 Response Factor (RF)

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

where: As = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cs = Concentration of the compound being measured (ug/l).
Cis = Concentration of the specific internal standard (ug/l).

10.2 Percent Relative Standard Deviation (% RSD)

$$\%RSD = \frac{SD}{RFav} \times 100$$

where: SD = Standard Deviation
RFav = Average response factor from initial calibration.

10.3 Percent Drift (%D).

$$\%D = \frac{(Cq - Cc)}{Cq} \times 100$$

where: Cq = Calibration Check Compound standard concentration.
Cc = Measured concentration using selected quantitation method.

10.4 Concentration (Conc.)

For water:

$$\text{Conc. (ug/l)} = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Vi}$$

For soil/sediment (on a dry weight basis):

$$\text{Conc. (ug/kg)} = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Ws \times M}$$

Where: Ac = Area of characteristic ion for compound being measured.
Vp = 5 ml (Total Purge Volume)
Vi = Initial volume of water purged (ml).
Ws = Weight of sample extracted (g).
M = (100 - % moisture in sample) / 100 or % solids / 100

10.5 Percent Recovery (% R)

$$\%R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

10.6 Relative Percent Difference (RPD)

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

Where: MSC = Matrix Spike Concentration
MSDC = Matrix Spike Duplicate Concentration

11.0 Documentation.

11.1 The Analytical Logbook records the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

11.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in the comments section.

11.2 Standards Preparation Logbook must be completed for all standard preparations. All information must be completed, the page must be signed and dated by the appropriate person.

11.2.1 The Accutest lot number must be cross referenced on the standard vial.

11.3 Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

12.0 Safety

The analyst should follow normal safety procedures as outlined in the Chemical Hygiene Plan.

Table 1

RECOMMENDED OPERATING CONDITION

Gas Chromatograph/ Mass Spectrometer

Carrier Gas(linear velocity)	Helium at 30 cm/sec
Mass range	35 - 300 amu
Electron Energy	70 volts (nominal)
Scan time	not to exceed 2 sec. per scan
Injection port temperature	200 - 225 C
Source temperature	200 - 250 C
Transfer line temperature	220 - 280 C
Analyzer temperature	220 - 250 C
Initial temperature	40 C
Time 1	3 minutes
Column temperature rate	8 degrees/min.
Final temperature	220 C.
Total run time	35 - 50 mins

Purge and Trap Unit

Purge time	11 min.
Dry Purge	3 min
Desorb preheat	100 C
Desorb	4 min. at 180 C
Bake	12 min. at 225 C
Transfer line	100 - 130 C
Valve temperature	approx. transfer line temperature

Table 2

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15-40 of mass 95
75	30-60 of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 198
175	5-9% of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Table 3

INTERNAL STANDARD QUANTITAION IONS

Internal Standard	Prim/Sec. Ions
1,4-Difluorobenzene	114 / 63,88
Chlorobenzene-d5	117 / 82, 119
Pentafluorobenzene	168
1,4-Dichlorobenzene-d4	152 / 115, 150

Table 4

SURROGATE RECOVERY LIMITS

Compound	(Prim/Sec. ions)	% Recovery (Water)	% Recovery (Soil)
Dibromofluorobenzene	(113)	86 - 118	80 - 120
Toluene-d8	(98)	88 - 110	81 - 117
4-Bromofluorobenzene	(95 / 174, 176)	86 - 115	74 - 121

Table 5

Criteria for CCC and SPCC

Initial Calibration: Maximum % RSD for CCC is 30 %

Continuing Calibration: Maximum % D for CCC is 20 %

Minimum acceptable average relative response factor (RRF) for SPCC is shown :

Calibration check compounds (CCC)

Volatile
Vinyl chloride
1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

System Performance Check Compounds (SPCC)

Compound name	Minium RF
Chloromethane	0.1
1,1-Dichloroethane	0.1
Bromoform	>0.1
1,1,2,2-Tetrachloroethane	0.3
Chlorobenzene	0.3

Table 6

QC ACCEPTANCE CRITERIA*

Compound	Test Conc. (ug/l)	Limit for s (ug/l)	Range for X (ug/l)	Range p,ps (%)
Benzene	20	6.9	15.2-26.0	37-151
Bromodichloromethane	20	6.4	10.1-28.0	35-155
Bromoform	20	5.4	11.4-31.1	45-169
Bromomethane	20	17.9	D-41.2	D-242
Carbon tetrachloride	20	5.2	17.2-23.5	70-140
Chlorobenzene	20	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	20	25.9	D-50.4	D-305
Chloroform	20	6.1	13.7-24.2	51-138
Chloromethane	20	19.8	D-45.9	D-273
Dibromochloromethane	20	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	20	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	20	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	20	7.1	11.8-34.7	18-190
1,1-Dichloroeethane	20	5.1	14.2-28.4	59-155
1,2-Dichloroethane	20	6.0	14.3-27.4	49-155
1,1-Dichloroethene	20	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	20	5.7	13.6-28.4	54-156
1,2-Dichloropropane	20	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	20	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	20	10.4	7.6-32.4	17-183
Ethyl benzene	20	7.5	17.4-26.7	37-162
Methylene chloride	20	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	20	7.4	13.5-27.2	46-157
Tetrachloroethene	20	5.0	17.0-26.6	64-148
Toluene	20	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	20	4.6	13.7-30.1	52-162
1,1,2-Trichlorethane	20	5.5	14.3-27.1	52-150
Trichloroethene	20	6.6	18.5-27.6	71-157
Trichlorofluoromethane	20	10.0	8.9-31.5	17-181
Vinyl chloride	20	20.0	D-43.5	D-251

s = Standard deviation of four recovery measurements, in ug/L.
X = Average recovery for four recovery measurements, in ug/L.
p, ps = Percent recovery measured.
D = Detected; result must be greater than zero.
* Criteria from 40 CFR part 136 for Method 624.

Table 7

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

This table contains a more extensive list than the lab's routine analyte list.

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Acetone	58	43
Acetonitrile	41	41, 40, 39
Acrolein	56	55,58
Acrylonitrile	53	52, 51
Allyl alcohol	57	57, 58, 39
Allyl chloride	76	76, 41, 39, 78
Benzene	78	-
Benzyl chloride	91	91, 126, 65, 128
Bromoacetone	136	43, 136, 138, 93,95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43, 72
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Buytlbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64	66
2-Chlorethanol	49	49, 44, 43, 51, 80
bis-(2-chloroethyl)sulfide	109	111, 158, 160
2-Chloroethyl-vinylether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
Chloroprene	53	53, 88, 90, 51

Table 7 (cont'd)

Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
3-Chloropropionitrile	54	54, 49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	75, 53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichlorethane	63	65, 63
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	79, 43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	55, 57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	88, 58, 43, 57
Epichlorohydrin	57	57, 49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	44, 43, 42
Ethyl methacrylate	69	69, 41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	44, 43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	43, 41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malonitrile	66	66, 39, 65, 38
Methacrylonitrile	41	41, 67, 39, 52, 66
Methyl acrylate	55	85

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	142, 127, 141
Methyl methacrylate	69	69, 41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	93, 66, 92, 78
Pentachloroethane	167	167, 130, 132, 165, 1
Propargyl alcohol	55	55, 39, 38, 53
6-Propiolactone	42	42, 43, 44
Propionitrile (ethyl cyanide)	54	54, 52, 55, 40
n-Propylamine	59	59, 41, 39

Table 7 (cont'd)

Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
4-Bromofluorobenzene	95	174, 176
Dibromofluoromethane	113	
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

Compound (1)	RDL (2)	RDL (2)
	Water	Soil
Acetone	10	10
Acetonitrile	100	10
Acrolein	5	5
Acrylonitrile	5	5
Allyl Chloride	100	10
Benzene	0.5	0.5
Benzyl Chloride	5	NA
Bromobenzene	5	1
Bromochloromethane	5	1
Bromodichloromethane	5	1
Bromoform	5	1
n-Butyl Alcohol	10	1
n-Butlybenzene	1	1
sec-Butylbenzene	1	1
tert-Butlybenzene	1	1
Chlorobenzene	5	1
Chlorodifluoromethane	5	1
Chloroethane	10	1
Chloroform	5	1
Chloroprene	5	1
o-Chlorotoluene	1	1
p-Chlorotoluene	1	1
2-Chloroethylvinylether	5	1
Carbon Disulfide	5	5
Carbon Tetrachloride	5	5
1,4-Dichlorobutane	5	5
1,1-Dichloroethane	5	5
1,1-Dichloroethylene	5	5
1,1-Dichloropropene	5	1
1,2-Dibromo-3-chloropropa	5	5
1,2-Dibromoethane	5	5
1,2-Dichloroethane	5	5
1,2-Dichloropropane	5	5
1,3-Dichloropropane	5	1
1,4-Dioxane	150	150
2,2-Dichloropropane	5	1
Dibromochloromethane	5	5
Dichlorodifluoromethane	5	5
cis- 1,2-Dichloroethylene	5	1
cis-1,3-Dichloropropene	5	5
m-Dichlorobenzene	1	1
o-Dichlorobenzene	1	1
p-Dichlorobenzene	1	1
p-Diethylbenzene	1	1
trans-1,2-Dichloroethylene	1	1
1,2-Dichloroethane(total)	1	1

Compound (1)	RDL (2) Water	RDL (2) Soil
trans-1,3-Dichloropropane	5	5
Ethyl Acetate	10	10
Ethylbenzene	1	1
Ethyl Ether	10	10
p-Ethyltoluene	1	1
Ethyl methacrylate	5	5
Freon 113	5	1
Freon 114	5	NA
2-Hexanone	50	50
Hexachlorobutadiene	1	1
Isopropylbenzene	1	1
p-Isopropyltoluene	1	1
Isobutyl alcohol	50	5
4-Methyl-2-Pentanone	50	5
Methacrylonitrile	5	5
Methyl Bromide Bromomet	10	5
Methyl Chloride-Chloromet	10	5
Methyl iodide-Iodomethane	5	5
Methyl methacrylate	5	5
Methlyene Bromide-Dibrom	5	5
Methylene Chloride	5	5
Methyl ethyl ketone-2Butan	100	100
MTBE	1	1
Methlynaphthalene (total)	5	5
Dimethylnaphthalene	5	5
Naphthalene	1	1
Pentachloroethane	5	5
Propionitrile	5	5
n-Propylbenzene	1	1
Styrene	5	5
1,1,1,2-Tetrachloroethane	5	5
1,1,1-Trichloroethane	5	5
1,1,2,2-Tetrachloroethane	5	5
1,1,2-Trichloroethane	5	5
1,2,3-Trichlorobenzene	1	1
1,2,3-Trichloropropane	5	5
1,2,4,5-Tetramethylbenzen	1	1
1,2,4-Trichlorobenzene	1	1
1,2,4-Trimethylbenzene	1	1
1,3,5-Trimethylbenzene	1	1
Tetrachloroethylene	5	1
Toluene	1	1
Trichloroethylene	5	1
Trichlorofluoromethane	5	5
trans-, 1,4-Dichloro-2-buten	5	5
Vinyl Chloride	10	10
Vinyl Acetate	5	5
Xylene (total)	1	1
m,p-xylene	1	1

Compound (1)	RDL (2)	RDL (2)
	Water	Soil
o-xylene	1	1
m-xylene	1	1
p-xylene	1	1

All values expressed in ppb.

(1) Compound list from List Definition Report.
(2) Current RDL.

Lab Manager: _____
QA Manager: _____

TEST NAME **DETERMINATION OF SEMIVOLATILE ORGANICS USING GC/MS SYSTEM**

METHOD REFERENCE SW-846 METHOD 8270B (Revision 2, September 1994)

1.0 SCOPE AND APPLICATION

1.1 The following method describes the analytical procedure which is utilized by Accutest to analyze semivolatile organic compounds in prepared from all types of solid waste matrices , soils, and ground water.

1.2 RDL (Reporting Detection Limit) may vary depending on matrix interferences, sample volumes or weight and percent moisture. The Method Detection Limit (MDL) is defined as the minimum concentration of a subtance that can be measured and reported with 99% confidence that the value is above zero. Refer to Table 6 for the compounds applicable to this method and their respective RDLs.

2.0 SUMMARY OF METHOD

2.1 This method is performed in accordance with the following extraction methodologies in SW-846, 3rd Edition : 3510, 3520, 3540, 3550 and 3580.

2.2 The resultant methylene chloride extract is injected into a tuned and calibrated GC/MS system equipped with a fused silica capillary column.

2.3 Direct injection of sample may be used in limited applications or wastes.

2.4 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.5 Once identified the compound is quantitated by internal standard techniques with an average response factor generated from a 5 point curve.

2.6 Additional unknown peaks with a response > 10 % of the closest internal standard may be processed through a library search with comparison to a data base of approximately 54,000 spectra. An estimated concentration is quantitated by assuming a response factor of 1.

3.0 INTERFERENCES

3.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

3.3 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent.

3.4 Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contaimnation.

4.0 SAMPLE PRESERVATION AND HOLDING TIME

4.1 PRESERVATION

4.1.1 Container - 1 liter glass bottle with teflon insert in cap.

4.1.2 Sample should be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus avoiding possible phthalate contamination.

4.1.3 The samples must be protected from light and refrigerated at 4° C from the time of receipt until extraction and analysis.

4.2 HOLDING TIME

4.2.1 Aqueous samples must be extracted within 7 days of sampling.

4.2.2 Soil, sediments and concentrated waste samples must be extracted within 14 days of sampling.

4.2.3 Extracts must be analyzed within 40 days following extraction.

5.0 APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

5.1.1 Gas Chromatograph.

The analytical system which is complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

The injection port is designed for splitless injection with capillary columns.

The capillary column is directly coupled to the source.

5.1.2 Column.

30 m x 0.25 mm fused silica (1 um film thickness) DB-5 or equivalent capillary column. Condition the column as per manufactures directions.

5.1.3 Mass Spectrometer.

Capable of scanning from 35-500 amu every second or less utilizing a 70 volt (nominal) electron energy in the electron impact ionization mode.
Capable of producing a mass spectrum which meets all the criteria in Table 2 when injecting 50 ng of Decafluorotriphenyl phosphine (DFTPP).

5.2 DATA SYSTEM

5.2.1 A computer system is interfaced to the mass spectrometer which allows the continuous acquisition and storage on machine readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

5.2.2 The computer utilizes software which allows searching any GC/MS data file for analytes which display specific fragmentation patterns.

5.2.3 The AQUARIUS and ENVIROQUANT data system is capable of quantitation using multipoint calibration and multipoint internal standards.

5.2.4 The recent version of the EPA/NIH/NBS mass spectral library (54,000 compounds) is being used.

5.2.5 Data can be archived to magnetic tape or disk for long term storage.

5.3 SYRINGE

5.3.1 10 ul graduated, manually held (Hamilton or equiv.).

5.3.2 10 ul graduated, auto sampler (Hamilton or equiv.).

6.0 REAGENTS AND STANDARDS

6.1 Solvents - Ultra pure, chromatography grade.

Methylene chloride, Methanol, and Acetone.

6.2 Stock standard solutions.

6.2.1 Commercially prepared standards used.

Supelco Supelpreme (or equivalent) mixtures at 2000 ug/ml of the following:

Base Neutrals.
- Base neutral mix 1.
- Base neutral mix 2.
- Polynuclear Aromatic Hydrocarbons mix.
- Benzidines mix.
- Hazardous Substances mix 2.
- Additonal requested compound(s) mix.

Acids.
- Phenols mix.
- Hazardous Substances mix 1.

6.2.2 DFTPP tune stock - Supelco: 25000 ug/ml or equivalent.

6.2.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

6.3 Internal Standard Solution.

The internal standard solution is prepared from commercially purchased standards. Refer to the standards preparation log for procedure. The solution will contain each standard at a concentrationof 4,000 ng/ul.

The internal standards are:
- 1,4-Dichlorobenzene-d4
- Naphthalene-d8
- Acenaphthene-d10
- Phenanthrene-d10
- Chrysene-d12
- Perylene-d12

6.3.1 Each 1 ml sample sample extract undergoung analysis should be spiked with 10 ul of the internal standard solution, resulting in a concentration of 40 ng/ul (ug/ml)of each internal standard.

6.3.2 Store at < 0 ° C when not being used.

6.4 Surrogate standard.

The base/neutral surrogate solution is prepared from commercially purchased standards to a final concentration of 100 ug/ml. Refer to standards preparation log book for procedure.

The compounds are:
- Nitrobenzene-d5.
- 2-Fluorobiphenyl.
- p-Terphenyl-d14.

The acid surrogate solution is prepared from commercially purchased standrads to a final concentration of 200 ug/ml.

The compounds are: Phenol-d6.
2-Fluorophenol.
2,4,6-Tribromophenol.

6.5 Calibration standards.

6.5.1 Calibration standards are prepared at the following concentration levels, including surrogates, from the stock standards.

The five levels : 20, 50, 80, 120, 160 ug/ml.

6.5.2 The concentration of surrogate shall be same at each calibration levels.
Base/Neutral : 100 ug/ml
Acid : 200 ug/ml

6.5.3 See Semivolatile Standard Prep. Logbook for preparation of working standard.

6.6 Decafluorotriphenylphosphine (DFTPP).

The DFTPP is prepared at 25 ug/ml in methylene chloride by diluting stock (6.2.2). Dilute 2 ul to 1000 ul for 50 ug/ml which is equivalent to 50 ng/ 1 ul injected.

6.7 Matrix spike solution.

The Base/Neutral matrix spike solution is prepared in methylene chloride at 200 ug/ml (refer to Table 8 for QC Criteria).

The Acid matrix spike solution is prepared in methylene chloride at 100 ug/ml (refer to Table 8 for QC Criteria).

7.0 CALIBRATION

7.1 The calibration range is covered by the standards : 20, 50, 80, 120, 160 ug/ml .

7.2 The linear range is covered by this calibration is 100% of highest concentration standard (up to 160 ug/ml).

7.3 Aliquot the proper amount of each calibration standard into a 2 ml crimp top vial.

7.4 The concentration of each internal standard is 40 ug/ml.

7.5 Each analyte is quantitatively determined using the closest eluting internal standard. (See Table 7.)

7.6 The Response Factor (RF) is defined in section 10.1.

7.6.1 The internal standards should permit most of the components of interest in a chromatogram to have retention times of 0.8 - 1.20 relative to one of the internal standards.

7.6.2 The base peak ions from the Table 7 are used as the primary ion for quantitation . If interferences are noted, the next most intense ion is used.

7.7 Initial calibration.

The following criteria must be met for the initial calibration to be valid.

7.7.1 The percent relative standard deviation (% RSD) (see section 10.2) of calibration check compound (CCC) (see Table 5) must be less than 30 %.

7.7.2 The minimum average RF of the system performance check compound (SPCC) (see Table 5) imust be 0.05.

7.7.3 For non CCC compounds, if the %RSD is >30%, the analyst must advise the team-leader or manager, the calibration may be accepted upon their approval.

7.8 Continuing calibration (CBCHK).

7.8.1 A continuing calibration check standard at mid-level concentration (80 ug/ml) must be acquired every 12 hrs.

7.8.2 The minimum RF of check standard for SPCC compounds must be 0.05.

7.8.3 The percent drift (% D, see section 10.3) for CCC must be less than 20.

7.8.4 If the CCCs are not required analytes by the permit, then all required analytes should meet the 20 %D.

7.8.5 All of the above criteria specified are met, the continuing calibration is considered valid.

7.8.6 If any of the criteria fail, a new five point calibration must be performed.

7.8.7 If any of the internal standard area change by a factor two (-50% to +100%) or retention time changes by more than 30 seconds from the last daily calibration check standard, the mass spectrometer must be inspected for malfunctions and corrections will be made, as appropriate.

8.0 PROCEDURE

8.1 Instrument conditions.

Recommended instrument conditions are listed in Table 1 Modifications are allowed as long as criteria of calibration are met.

8.2 Sample preparation.

Refer to the appropriate extraction SOP.

8.3 Daily GC/MS performance check.

8.3.1 Every 12 hours, inject 1 ul (50 ng) of DFTPP solution directly on to the column.

8.3.2 The GC/MS system must be checked to verify that acceptable performance criteria are achieved (see Table 2).

8.3.3 This performance test must be passed before any samples, blanks or standards are analyzed.

8.3.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are met.

8.3.5 The injection time of the acceptable tune analysis, is considered the start of the 12 hour clock.

8.4 Daily calibration check.

See section 7.8.

8.5 Sample analysis.

8.5.1 The internal standard (I.S.) must be added to sample extract and mixed thoroughly, immediately before injection into the instrument. This minimizes losses due to adsorption, chemical reaction or evaporation.

8.5.2 The concentration of each I.S. is 40 ug/ml. Add 10 ul of 4000 ug/ml into 1 ml extract.

8.5.3 Inject 1 ul of the sample extract.

8.5.4 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and re-analyze.

8.5.5 When the extracts are not being used for the analyses, store them at 4° C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

8.6 Data interpretation.

8.6.1 Qualitative identification.

The targeted compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The criteria required for a positive identification are:

8.6.1.1 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criteria is the RRT of sample component must be within ± 0.06 RRT units of the standard.

8.6.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10 % (major abundant ion in the spectrum equals 100 %) should be present in the sample spectrum.

8.6.1.3 The relative intensities of these ion must agree within ± 30 % between the daily standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 20 and 80 %.

8.6.1.4 Structural isomers that produce very similar mass specrtra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficiently GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 % of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

8.6.2 Quantitative analysis.

8.6.2.1 When a target compound has been identified, concentration (see section 10.4) will be based on the integrated area of the quantitation ion, which is normally the base peak.

8.6.2.2 The sample may produce an interference for the primary ion. This may be characterized by an excessive background signal of the same ion which distorts the peak shape beyond a definitive integration. The interference could also, severely inhibit the response of the internal standard ion. If an interference is apparent the secondary ion must be used to generate a new calibration factor.

8.7 Library search for tentatively identified compounds.

If a library search is requested, the analyst should perform a forward library search of the NBS mass spectral library to tentatively identify 10 to 15 non-reported compounds (15 for base, 10 for acid, 25 for base/acid fraction).

Guidelines for making tentative identification are:

8.7.1 These compounds should have a response greater than 10 % of the nearest internal standard. The response is obtained from the Total Ion Chromatogram .

8.7.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

8.7.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

8.7.4 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

8.7.5 The relative intensities the major ions should agree within ± 20 %.

8.7.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

8.7.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

8.7.8 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

8.7.9 Quantitation will be performed on the nearest internal standard.

9. QUALITY CONTROL

QC Requirements Summary.

DFTPP	Every 12 hrs.
Calibration Check std.	Every 12 hrs.
Batch blank	one per analytical batch* or one per extraction batch.
Matrix Spike	one per analytical batch*.
Matrix Spike Duplicate	one per analytical batch*.
Blank Spike (QC Reference)	one per analytical batch*.
Leachate Spike	one per leachate batch.
Leachate Blank	one per leachate batch.
Surrogate	every sample and standard.
Internal Standard	every sample and standard.

* A batch is defined as a maximum of 20 samples, or SDG, whichever is more frequent.

9.1 Daily GC/MS performance check - refer to section 8.3.

9.2 Daily calibration check - refer to section 7.8.

9.3 Method blank.

9.3.1 The method blank is carried through all stages of the sample preparation and measurement.

9.3.2 An acceptable method blank must be analyzed once for each extraction batch.

9.3.3 No compound can be present above the RDL.. SeeTable 6 for RDLs.

9.3.4 Surrogates must meet Table 4 criteria. If the method blank does not meet surrogate criteria or contains target compounds above the RDL it must be reanalyzed. If the reanalysis confirms the original data the entire batch should

be re-extracted.

9.4 Matrix Spike(MS) / Matrix Spike Duplicate(MSD) / Blank spike

9.4.1 One sample from each analytical batch is selected and spiked in duplicate with select compounds to check precision and reproducibility.

9.4.2 Matrix spikes are prepared by spiking an actual sample at a concentration of 100 ug/l for base/neutral and 200 ug/l for acids.

9.4.3 Percent recoveries (%.R) (see section 10.5) are compared to the acceptance criteria listed in Table 8*.

(*) Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 2SP.

9.4.4 A relative percent deviation (RPD) (see section 10.6) is calculated and compared to RPD levels presented in Table 6.

9.4.5 If matrix spike recoveries do not meet criteria (see Table 8) and the QC check sample (blank spike) does meet the acceptance criteria, matrix interference is to be assumed and the data is reportable.

9.5 Surrogate

9.5.1 All blanks, samples, and matrix spikes contain surrogate compounds which are used to monitor method performance.

9.5.2 If the recovery of any surrogate compounds does not meet the control limits specified in Table 4 it will be flagged and:

Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 3SP.]

9.5.2.1 The calculation, standards and instrument must be checked for error.

9.5.2.2 The sample may be reanalyzed if a problem is identified in 9.5.2.1.

9.5.2.3. Reextract and reanalyze or qualify the result.

9.5.4 The above conditions are not required for samples having matrix interference problems. If a visible matrix interference effect is observed, defined as excessive signal where target or non-target responses are greater than the response of the internal standards, the surrogates will be qualified as outside the limits due to matrix interference.

9.5.5 If surrogate recoveries are acceptable upon reanalysis (9.5.2.2), the data from the reanalysis is reported. If the sample is re-extracted and the second extraction date did not meet the hold time, then both sets of data will be submitted.

9.5.6 If the surrogates are still outside control limits upon re-extraction and reanalysis, then both sets of data should be submitted with the first analysis reported.

9.6 Internal Standard.

9.6.1 Retention time for all internal standard must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 80 ug/ml standard of initial calibration.

9.6.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area of the latest calibration standard (12 hr time period).

9.6.3 If the area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

9.6.4 If the areas are acceptable upon reanalysis, the reanalysis data is reported.

9.6.5 If the areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

10. CALCULATION

10.1 Response Factor (RF).

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

where: As = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cs = Concentration of the compound being measured (ug/ml).
Cis = Concentration of the specific internal standard (ug/ml).

10.2 Percent Relative Standard Deviation (%RSD).

$$\%RSD = \frac{SD}{RFav} \times 100$$

where: SD = Standard Deviation.
RFav = Average response factor from initial calibration.

10.3 Percent Drift (%D).

$$\%D = \frac{(Cq - Cc)}{Cq} \times 100$$

where: Cq = Calibration Check Compound standard concentration.
Cc = Measured concentration using selected quantitation method.

10.4 Concentration (Conc.).

for water:

$$\text{Conc. (ug/l)} = \frac{Ac \times Cis \times Vf \times D \times 1000}{Ais \times RFav \times Vi}$$

for soil/sediment (on a dry weight basis):

$$\text{Conc. (ug/Kg)} = \frac{Ac \times Cis \times Vf \times D \times 1000}{Ais \times RFav \times Ws \times M}$$

where: Ac = Area of characteristic ion for compound being measured.
Vf = Final Volume of total extract (ml).
D = Secondary dilution factor.
Vi = Initial volume of water extracted (ml).
Ws = Weight of sample extracted (g).
M = (100 - % moisture in sample) / 100.

10.5 Percent Recovery (%R).

$$\%R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

10.6 Relative Percent Difference (RPD).

$$RPD = \frac{(MSC - MSDC)}{(1/2)(MSC+MSDC)} \times 100$$

where: MSC = Matrix Spike Concentration.
MSDC = Matrix Spike Duplicate Concentration.

11.0 Documentation.

11.1 Analytical Logbook records the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

11.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in the comments section.

11.2 Standards Preparation Logbook must be completed for all standard preparations. All information must be completed, the page must be signed and dated by the appropriate person.

11.2.1 The Accutest lot number must be cross referenced on the standard vial.

11.3 Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

12.0 Safety

The analyst should follow safety procedures as outlined in the Chemical Hygiene Plan.

Table 1

Recommended Operating Conditions

Injection Type	Spiltless
Purge Off Time	0.8 min.
Carrier Gas(linear velocity)	Helium at 30 cm/sec
Septum Purge Flow	1 ml/min
Mass Range	35-500 amu
Electron Energy	70 volts (nominal)
Scan Time	not to exceed 1 sec.
Injection Port Temp.	250-300 °C
Source temp.	220-270 °C
Transfer Line Temperature	250-300 °C
Analyzer Temp	220-250 °C
Initial temp.	50 °C
Time 1	4 minutes
Column Temp Rate	8 degrees/min
Final Temp	290-320 °C according to column type
Total run time	40-70 min

Table 2

DFTPP KEY IONS ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60 % of mass 198
197	<1% of mass 198
198	Base peak, 100% of relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

Table 3

Internal Standards

Internal Standard	Prim/Sec Ions
1,4-Dichlorobenzene-d4	152/150, 115
Naphthalene-d8	136 / 68
Acenaphthene-d10	164 / 162, 160
Phenanthrene-d10	188 / 94, 80
Chrysene-d12	240 / 120, 236
Perylene-d12	264 / 260, 265

Table 4

Surrogate
Compounds and Criteria

Compound	Prim/Sec Ions	QC Limits	
		Water ug/l	Soil ug/kg
Base/Neutrals		%	%
Nitrobenzene-d5	82 / 128, 65	35-114	23-120
2-Fluorobiphenyl	172 / 171	43-116	30-115
Terphenyl-d14	244 / 122, 212	33-141	18-137
Acids			
2-Fluorophenol	112 / 64	21-100	25-121
Phenol-d6	99 / 42,71	10-94	24-113
2,4,6-Tribromophenol	330 / 332, 141	10-123	19-122

Table 5

Criteria for CCC and SPCC Compounds

A. Calibration Check Compounds (CCCs)

Initial Calibration: Maximum % RSD for CCC is 30%.

Continuing Calibration: Maximum %D for CCC is 20%.

Base Neutral	Acid
1,4-Dichlorobenzene	Phenol
Hexachlorobutadiene	2,4-Dichlorophenol
Acenaphthene	2-Dinitrophenol
Fluoranthene	p-Chloro-m-cresol
N-Nitrosodiphenylamine	2,4,6-Trichlorophenol
Di-n-octyl phthalate	Pentachlorophenol
Benzo (a) pyrene	

B. System Performance Check Compounds (SPCCs)

Minimum acceptable average relative response factor (RRF) is 0.050 for SPCCs.

BaseNeutral	Acid
N-Nitroso-di-n-propylamine	2,4-Dinitrophenol
Hexachlorocyclopentadiene	4-Nitrophenol

Table 6

Compound (1)	RDL	RDL
	Water	Soil
	ug/l	ug/kg
Benzenthiol	10	10
Benzoic Acid	2	10
2-Chlorophenol	1.7	2.9
4-Chloro-3-methyl phenol	1.2	3.2
2,4-Dichlorophenol	1.8	3.6
2,4-Dimethylphenol	2.8	4.5
2,4-Dinitrophenol	1.3	7.6
2,6-Dinitrophenol	10	10
4,6-Dinitro-o-cresol	1.1	3.6
Dinoseb	10	10
2-Methlyphenol	1.7	3.8
3 & 4-Methylphenol	2.4	4.5
4-Methylphenol	2.4	4.5
2-Nitrophenol	2.4	4.5
4-Nitrophenol	0.77	5.7
Pentachlorophenol	1.2	3.8
Phenol	0.67	2.9
2,3,4,6-Tetrachlorophenol	10	10
2,4,5-Trichlorophenol	1.5	2.9
2,4,6-Trichlorophenol	1	2.7
2-Acetylaminofluorene	10	10
4-Aminobiphenyl	10	10
Acenaphthene	1.1	1.2
Acenaphthylene	1.2	1.2
Acetophenone	10	10
Aniline	10	10
Anthracene	1.6	1.2
Aramite	10	10
A,A-dimethylphenethylamine	10	10
Benzidine	1.7	50
Benzo(a)anthracene	1.2	0.88
Benzo(a)pyrene	1.2	1.1
Benzo(b)fluoranthene	2.5	1.2
Benzo(g,h,i)perylene	1.5	0.79
Benzo(k)fluoranthene	1.8	2.4
4-Bromophenyl phenyl ether	1.8	1
Butyl benzyl phthalate	2.1	0.41
Benzyl Alcohol	20	20
Benzo(B+J+K)fluoranthene	10	10
Cumene	10	10
2-chloronaphthalene	1.2	1.6
4-Chloroaniline	1.6	1.5
Carbazole	2	1.1
Chlorobenzilate	10	10
Chrysene	0.83	0.67
bis(2-Chloroethoxy)methane	1.6	1.6
bis(2-Chloroethyl)ether	1.2	1.1

Table 6

Compound (1)	RDL	RDL
	Water	Soil
	ug/l	ug/kg
bis(2-Chloroisopropyl)ether	1.3	1.3
4-Chlorophenyl phenyl ether	1	1.6
1,2-Dichlorobenzene	1.1	1.5
1,2-Diphenylhydrazine	1.8	1.2
1,3-Dichlorobenzene	1.5	0.92
1,4-Dichlorobenzene	1.5	1.2
1,4-Dinitrobenzene	10	10
2,4-Dinitrotoluene	0.95	2.6
2,6-Dinitrotoluene	1	1.7
3,3'-Dichlorobenzidine	1.6	2.2
3,3'-Dimethylbenzidine	10	10
7,12-Dimethylbenz(a)anthracene	10	10
Diallate	10	10
Dibenz(a,h)acridine	10	10
Dibenzo(a,h)anthracene	1.4	1.1
Dibenzofuran	1.3	0.99
Dimethoate	10	10
Diphenylamine	10	10
Disulfoton	10	10
m-Dinitrobenzene	10	10
p - (Dimethylamine)azobenzene	10	10
Di-n-butyl phthalate	2.2	0.68
Di-n-octyl phthalate	1.6	0.84
Diethyl phthalate	2.7	1
Dimethyl phthalate	3	0.99
bis(2-Ethylhexyl)phthalate	2.1	0.98
Ethyl methanesulfonate	10	10
Famphur	10	10
Fluoranthene	1.3	0.79
Fluorene	1.2	1.1
Hexachlorobenzene	1.9	1.7
Hexachlorobutadiene	1.5	1.3
Hexachlorocyclopentadiene	0.62	2.4
Hexachloroethane	1.1	2.2
Hexachloropropene	10	10
Indene	10	10
Indeno(1,2,3-cd) pyrene	1.7	0.55
Isodrin	10	10
Isophrone	1.4	1.6
Isosafrole	10	10
Kepone	10	10
1-Methylnaphthalene	10	10
2-Methylnaphthalene	2	10
3-Methylcholanthrene	10	10
4,4'methylenebis(2-chloroaniline)	10	10
Methapyrilene	10	10
Methyl Methanesulfonate	10	10

Table 6

Compound (1)	RDL	RDL
	Water	Soil
	ug/l	ug/kg
Methyl Parthion	10	10
Methyl Chrysene	10	10
1,4-Naphthoquinone	10	10
1-Naphthylamine	10	10
2-Naphthylamine	10	10
2-Nitroaniline	0.85	1.7
3-Nitroaniline	0.8	1.8
4-Nitroaniline	0.43	1.1
5-Nitro-o-toluidine	10	10
Naphthalene	1.6	1.6
Nitrobenzene	1.3	1.5
n-Nitrosodimethylamine	1.1	2.7
4-Nitroquinoline 1-oxide	10	10
N-Nitroso-di-n-propylamine	1.6	1.7
N-Nitrosodi-n-butylamine	10	10
N-Nitrosodiethylamine	10	10
N-Nitrosodiphenylamine	2	0.71
N-Nitrosodimethylethylamine	10	10
N-Nitrosomorpholine	10	10
N-Nitrosopiperidine	10	10
N-Nitrosopyrrolidine	10	10
o,o,o-Triethyl phosphorothioate	10	10
2-Picoline	10	10
Parathion	10	NA
Pentachlorobenzene	10	10
Pentachloronitrobenzene	10	10
Phenacetine	10	10
Phenanthrene	2.1	0.[illegible]
Phorate	10	10
Pronamide	10	10
Pyrene	1.6	0.59
Pyridine	10	10
p-Phenylenediamine	10	10
Quinoline	10	10
Safrole	10	10
1,2,4,5-Tetrachlorobenzene	10	10
1,2,4-Trchlorobenzene	1.6	1.3
Thionazine	10	10
o-Toluidine	10	10
sym-Trinitrobenzene	10	10
Tetraethyl dithiopyrophosphate	10	NA
Dimethylnaphthalene	NA	NA
2,2'Oxybis(1-Chloropropane)	NA	NA

(1) List taken from List-Definition.
This list is more extensive than the routine reporting list.
Refer toTable 9 for the routine reporting list.

Table 7

Internal Standards and Quanitation Ion

Internal Standard	Compound	Ions
1,4-Dichlorobenzene-d4	Aniline	93/66,65
	Benzyl Alcohol	108/79,77
	Bis(2-chloroethyl)ether	93/63,95
	2-Chlorophenol	128 / 64, 130
	1,3-Dichlorobenzene	146 / 148, 111
	1,4-Dichlorobenzene	146 / 148, 111
	1,2-Dichlorobenzene	146 / 148, 111
	Ethyl methanesulfonate *	79 / 109,97
	2-Fluorophenol (surr)	
	Hexachlorethane	117 / 201, 199
	Methyl methanesulfonate *	80 / 79, 64
	2-Methylphenol	108 / 107, 79
	4-Methylphenol	108 / 107, 79
	N-nitrosodimethylamine	74 / 42
	N-nitroso-di-n-propylamine	70 / 101, 130
	Phenol-d6 (surr)	
	2-Picoline *	93 / 66, 92
Naphthalene-d8	Acetophenone *	105 / 77, 51
	Benzoic Acid	184 / 92, 185
	Bis(2-chloroethoxy)methane	93 / 95, 123
	4-Chloro-methylphenol	107 / 144
	2,4-Dichlorophenol	162 / 164, 98
	2,6-Dichlorophenol *	162 / 164, 98
	2,4-Dimethylphenol	122 / 107
	a,a-Dimethyl-phenethylamine	58 / 91, 42
	Hexachlorobutadiene	225 / 223, 227
	Isophorone	82 / 95, 138
	2-Methylnaphthalene	142 / 141
	Naphthalene	128 / 129, 127
	Nitrobenzene	77 / 123, 65
	Nitrobenzene-d* (surr)	
	N-nitroso-di-n-butylamine	84 / 57 / 41
	2-Nitrophenol	139 / 109, 65
	N-nitrosopiperidine *	42 / 114, 55
	1,2,4-Trichlorobenzene	180 / 182, 145
Acenaphthene-d10	Acenaphthene	154 / 153, 152
	Acenaphthylene	152 / 151, 153
	1-Chloronaphthalene *	162 / 127, 164
	2-Chloronaphthalene	162 / 127, 164
	4-Chlorophenylphenylether	204 / 206, 141
	Dibenzofuran	168 / 139
	Diethyl phthalate	149 / 177, 150
	Dimethyl phthalate	163 / 149, 164
	2,4-Dinitrophenol	184 / 63, 154
	2,4-Dinitrotoluene	165 / 63, 89
	2,6-Dinitrotoluene	165 / 63, 89
	Fluorene	166 / 165, 167

Table 7

Internal Standards and Quanitation Ion

Internal Standard	Compound	Ions
Acenaphthene-d10	Hexachlorocyclopentadiene	237 / 235, 272
(cont'd)	2-Fluorobiphenyl (surr)	
	1-Naphthylamine *	143 / 115, 116
	2-Naphthylamine *	143 / 115, 116
	2-Nitroaniline	65 / 92, 138
	3- Nitroaniline	138 / 108, 92
	4- Nitroaniline	138 / 108, 92
	4-Nitrophenol	139/ 109, 65
	Pentachlorobenzene	250 / 252, 248
	1,2,4,5-Tetrachlorobenzene *	216 / 214, 218
	2,3,4,6-Tetrachlorophenol	232 / 230, 131
	2,4,6-Tribromophenol (surr)	
	2,4,6-Trichlorophenol	196 / 198, 200
	2,4,5-Trichlorophenol	196 / 198, 200
Phennathrene-d10	4-Aminobiphenyl	169 / 168, 170
	Anthracene	178 / 176, 179
	4-Bromophenyl phenyl ether	248 / 250, 141
	Di-n-butyl phthalate	149 / 150
	4,6-Dinitro-2-methylphenol	198 / 51, 105
	Diphenylamine *	169 / 168, 167
	1,2-Diphenylhydrazine	77 / 105
	Fluoranthene	202 / 101, 203
	Hexachlorobenzene	284 / 142, 249
	N-nitrosodiphenylamine	169 / 168, 167
	Pentachlorophenol	266 / 264, 268
	Phenacetin *	108, 109, 179
	Phenanthrene	178 / 179, 176
	Pronamide *	173 / 175, 145
Chrysene-d12	Benzidine	184 / 92, 185
	Benzo(a)anthracene	228 / 229 / 226
	Bis(2-ethylhexyl)phthalate	149 / 167, 279
	Butylbenzyl phthalate	149 / 91
	Chrysene	228 / 226, 229
	3,3'Dichlorobenzidine	252 / 254, 126
	p-Dimethylaminoazobenzene *	120 /225, 77
	Pyrene	202 / 200, 203
	Terphenyl-d14 (surr)	
Perylene-d12	Benzo(b)fluoranthene	252 / 125
	Benzo(k)fluoranthene	252 / 125
	Benzo(g,h,i)perylene	276 / 138, 277
	Dibenz(a,h)anthracene	278 / 139, 279
	7,12-Dimethylbenz(a)anthracene	256 / 241, 257
	Indeno(1,2,3-d)pyrene	276
	3-Methylchloanthrene	268 / 253

(*) Not a routine target compound.

Table 8

MS/MSD Criteria

Compound (1)	QC Limits:	
	MS/MSD	RPD
	%	%
Acenaphthene	47-145	30
Acenaphthylene	33-145	30
Aniline	1-150	30
Anthracene	27-133	30
Benzidine	1-150	30
Benzo(a)anthracene	33-143	30
Benzo(a)pyrene	17-163	30
Benzo(b)fluoranthene	24-159	30
Benzo(g,h,i)perylene	0-210	30
Benzo(k)fluoranthene	11-162	30
4-Bromophenyl phenyl ether	53-127	30
Butyl benzyl phthalate	0-152	30
Benzyl Alcohol	1-150	30
Cumene	1-150	30
2-chloronaphthalene	60-118	30
4-Chloroaniline	1-150	30
Carbazole	1-150	30
Chrysene	17-168	30
bis(2-Chloroethoxy)methane	33-184	30
bis(2-Chloroethyl)ether	12-158	30
4-Chlorophenyl phenyl ether	25-158	30
1,2-Dichlorobenzene	32 - 129	30
1,2-Diphenylhydrazine	1-150	30
1,3-Dichlorobenzene	0-172	30
1,4-Dichlorobenzene	20-124	30
2,4-Dinitrotoluene	39-139	30
2,6-Dinitrotoluene	50-158	30
3,3'-Dichlorobenzidine	0-262	30
Dibenzo(a,h)anthracene	0-227	30
Dibenzofuran	1-150	30
Di-n-butyl phthalate	1-118	30
Di-n-octyl phthalate	4-146	30
Diethyl phthalate	0-114	30
Dimethyl phthalate	0-112	30
bis(2-Ethylhexyl)phthalate	8-158	30
Fluoranthene	26-137	30
Fluorene	59-121	30
Hexachlorobenzene	0-152	30
Hexachlorobutadiene	24-116	30
Hexachlorocyclopentadiene	1-150	30
Hexachloroethane	40-113	30
Indeno(1,2,3-cd) pyrene	0-171	30
Isophrone	21-196	30
1-Methylnaphthalene	1-150	30
2-Methylnaphthalene	1-150	30
2-Nitroaniline	1-150	30

Table 8

MS/MSD Criteria

Compound (1)	QC Limits:	
	MS/MSD	RPD
	%	%
3-Nitroaniline	1-150	30
4-Nitroaniline	1-150	30
Naphthalene	21-133	30
Nitrobenzene	35-180	30
N-Nitroso-di-n-propylamine	41-230	30
N-Nitrosodiphenylamine	1-150	30
N-Nitrosodimethylethylamine	0-230	30
Phenanthrene	54-120	30
Pyrene	52-115	30
Pyridine	1-150	30
1,2,4-Trchlorobenzene	44-142	30
Dimethylnaphthalene	1-150	30
2,2'Oxybis(1-Chloropropane)	36-166	30

TABLE 9_ Routine Reporting List

Report of Analysis

Client Sample ID:			
Lab Sample ID:	E15026-1	**Date Sampled:**	10/02/96
Matrix:	AQ - Water	**Date Received:**	10/02/96
Method:	SW846 8270	**Percent Solids:**	n/a
Project:			

	File ID	DF	Analyzed	By	Prep Date	Prep Batch	Analytical Batch
Run #1	F5372.D	1	10/03/96	SDF	10/03/96	OP1476	EF982
Run #2							

ABN TCL List

CAS No.	Compound	Result	RDL	Units	Q
65-68-0	Benzoic Acid	ND	2.0	ug/l	
95-57-8	2-Chlorophenol	ND	1.7	ug/l	
59-50-7	4-Chloro-3-methyl phenol	ND	1.2	ug/l	
120-83-2	2,4-Dichlorophenol	ND	1.8	ug/l	
105-67-9	2,4-Dimethylphenol	ND	2.8	ug/l	
51-28-5	2,4-Dinitrophenol	ND	1.3	ug/l	
534-52-1	4,6-Dinitro-o-cresol	ND	1.1	ug/l	
95-48-7	2-Methylphenol	ND	1.7	ug/l	
	3&4-Methylphenol	ND	2.4	ug/l	
88-75-5	2-Nitrophenol	ND	2.4	ug/l	
100-02-7	4-Nitrophenol	ND	0.77	ug/l	
87-86-5	Pentachlorophenol	ND	1.2	ug/l	
108-95-2	Phenol	ND	0.67	ug/l	
95-95-4	2,4,5-Trichlorophenol	ND	1.5	ug/l	
88-06-2	2,4,6-Trichlorophenol	ND	1.0	ug/l	
83-32-9	Acenaphthene	ND	1.1	ug/l	
208-96-8	Acenaphthylene	ND	1.2	ug/l	
120-12-7	Anthracene	ND	1.6	ug/l	
56-55-3	Benzo(a)anthracene	ND	1.2	ug/l	
50-32-8	Benzo(a)pyrene	ND	1.2	ug/l	
205-99-2	Benzo(b)fluoranthene	ND	2.5	ug/l	
191-24-2	Benzo(g,h,i)perylene	ND	1.5	ug/l	
207-08-9	Benzo(k)fluoranthene	ND	1.8	ug/l	
101-55-3	4-Bromophenyl phenyl ether	ND	1.8	ug/l	
85-68-7	Butyl benzyl phthalate	ND	2.1	ug/l	
100-51-6	Benzyl Alcohol	ND	20	ug/l	
91-58-7	2-Chloronaphthalene	ND	1.2	ug/l	
106-47-8	4-Chloroaniline	ND	1.6	ug/l	
218-01-9	Chrysene	ND	0.83	ug/l	
111-91-1	bis(2-Chloroethoxy)methane	ND	1.6	ug/l	
111-44-4	bis(2-Chloroethyl)ether	ND	1.2	ug/l	
108-60-1	bis(2-Chloroisopropyl)ether	ND	1.3	ug/l	
7005-72-3	4-Chlorophenyl phenyl ether	ND	1.0	ug/l	
95-50-1	1,2-Dichlorobenzene	ND	1.1	ug/l	
541-73-1	1,3-Dichlorobenzene	ND	1.5	ug/l	
106-46-7	1,4-Dichlorobenzene	ND	1.5	ug/l	

ND = Not detected
RDL = Reported Detection Limit
E = Indicates value exceeds calibration range
J = Indicates an estimated value
B = Indicates that analyte is found in associated method blank
N = Indicates presumptive evidence of a compound

Report of Analysis

Client Sample ID:			
Lab Sample ID:	E15026-1	**Date Sampled:**	10/02/96
Matrix:	AQ - Water	**Date Received:**	10/02/96
Method:	SW846 8270	**Percent Solids:**	n/a
Project:			

	File ID	DF	Analyzed	By	Prep Date	Prep Batch	Analytical Batch
Run #1	F5372.D	1	10/03/96	SDF	10/03/96	OP1476	EF982
Run #2							

ABN TCL List

CAS No.	Compound	Result	RDL	Units	Q
121-14-2	2,4-Dinitrotoluene	ND	0.95	ug/l	
606-20-2	2,6-Dinitrotoluene	ND	1.0	ug/l	
91-94-1	3,3'-Dichlorobenzidine	ND	1.6	ug/l	
53-70-3	Dibenzo(a,h)anthracene	ND	1.4	ug/l	
132-64-9	Dibenzofuran	ND	1.3	ug/l	
84-74-2	Di-n-butyl phthalate	ND	2.2	ug/l	
117-84-0	Di-n-octyl phthalate	ND	1.6	ug/l	
84-66-2	Diethyl phthalate	ND	2.7	ug/l	
131-11-3	Dimethyl phthalate	ND	3.0	ug/l	
117-81-7	bis(2-Ethylhexyl)phthalate	ND	2.1	ug/l	
206-44-0	Fluoranthene	ND	1.3	ug/l	
86-73-7	Fluorene	ND	1.2	ug/l	
118-74-1	Hexachlorobenzene	ND	1.9	ug/l	
87-68-3	Hexachlorobutadiene	ND	1.5	ug/l	
77-47-4	Hexachlorocyclopentadiene	ND	0.62	ug/l	
67-72-1	Hexachloroethane	ND	1.1	ug/l	
193-39-5	Indeno(1,2,3-cd)pyrene	ND	1.7	ug/l	
78-59-1	Isophorone	ND	1.4	ug/l	
91-57-6	2-Methylnaphthalene	ND	2.0	ug/l	
88-74-4	2-Nitroaniline	ND	0.85	ug/l	
99-09-2	3-Nitroaniline	ND	0.80	ug/l	
100-01-6	4-Nitroaniline	ND	0.43	ug/l	
91-20-3	Naphthalene	ND	1.6	ug/l	
98-95-3	Nitrobenzene	ND	1.3	ug/l	
621-64-7	N-Nitroso-di-n-propylamine	ND	1.6	ug/l	
86-30-6	N-Nitrosodiphenylamine	ND	2.0	ug/l	
85-01-8	Phenanthrene	ND	2.1	ug/l	
129-00-0	Pyrene	ND	1.6	ug/l	
120-82-1	1,2,4-Trichlorobenzene	ND	1.6	ug/l	

CAS No.	Surrogate Recoveries	Run# 1	Run# 2	Limits
367-12-4	2-Fluorophenol	54%		21-100%
4165-62-2	Phenol-d5	42%		10-94%
118-79-6	2,4,6-Tribromophenol	104%		10-123%
4165-60-0	Nitrobenzene-d5	75%		35-114%

ND = Not detected
RDL = Reported Detection Limit
E = Indicates value exceeds calibration range
J = Indicates an estimated value
B = Indicates that analyte is found in associated method blank
N = Indicates presumptive evidence of a compound

Report of Analysis

Client Sample ID:			
Lab Sample ID:	E15026-1	**Date Sampled:**	10/02/96
Matrix:	AQ - Water	**Date Received:**	10/02/96
Method:	SW846 8270	**Percent Solids:**	n/a
Project:			

	File ID	DF	Analyzed	By	Prep Date	Prep Batch	Analytical Batch
Run #1	F5372.D	1	10/03/96	SDF	10/03/96	OP1476	EF982
Run #2							

ABN TCL List

CAS No.	Surrogate Recoveries	Run# 1	Run# 2	Limits
321-60-8	2-Fluorobiphenyl	83%		43-116%
1718-51-0	Terphenyl-d14	83%		33-141%

ND = Not detected
RDL = Reported Detection Limit
E = Indicates value exceeds calibration range
J = Indicates an estimated value
B = Indicates that analyte is found in associated method blank
N = Indicates presumptive evidence of a compound

Lab Mgr. _____
QA Mgr. _____

TEST NAME DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBs USING GC SYSTEM

METHOD REFERENCE SW-846 - 8080A (Revision 1, September 1994);

1.0 SCOPE AND APPLICATION

1.1 The following method describes the analytical procedures which are utilized by Accutest to acquire samples for analysis of organochlorine pesticides and polychlorinated biphenyls (PCBs) by gas chromatography with an Electron Capture Detector (ECD).

1.2 RDL (Reporting Detection Limit) is based on Accutest laboratory extraction procedure and lowest calibration standard. RDLs may vary depending on matrix difficulties and sample volumes or weight and percent moisture. The RDL is equivalent to the laboratory's MDL (Method Detection Limit).

1.3 The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence. The MDL is evaluated per SOP QC001.

2.0 SUMMARY OF METHOD

2.1 This method is performed in accordance with EPA Extraction Methods : 3510, 3520, 3540 and 3550 SW-846 September, 1994. Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. Refer to extraction SOP.

2.2 The following cleanups may be used to eliminate interferences in the analysis: Alumina column cleanup (Method 3610), Florisil column cleanup (Method 3620), and Sulfur Cleanup (Method 3660). Refer to extraction SOP.

2.3 The resultant hexane extract is injected into a calibrated GC system containing a fused silica capillary column.

2.4 The peaks detected are qualitated by comparison to retention times specific to the known target list of compounds on two different column types (primary and confirmation).

2.5 Once identified the compound is quantitated by external standard techniques with an average calibration factor generated from a 5 point curve.

3.0 INTERFERENCES

3.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary from source to source. Interferences such as sulfur and phthalate are treated with copper and alumina by organics preparation respectively.

COPY
3 OF 3

4.0 SAMPLE PRESERVATION AND HOLDING TIME

4.1 PRESERVATION

4.1 1 Container-1 liter glass bottle with Teflon insert in cap.

4.1.2 Sample should be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing possible phthalate contamination.

4.1.3 The samples must be protected from light and refrigerated at 4°C from the time of receipt until extraction and analysis.

4.2 HOLDING TIME

4.2.1 Aqueous sample must be extracted within 7 days of sampling.

4.2.2 Soil sample must be extracted within 14 days of sampling.

4.2.3 Extracts must be analyzed within 40 days following extraction.

5.0 APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH SYSTEM

5.1.1 Gas Chromatograph.

The analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

The injection port is designed for splitless injection with capillary columns.

The capillary column is directly coupled to the detector.

5.1.2 Columns:

Column 1 — 30 m x 0.32m fused silica (1 um film thickness) DB-1701 wide-bore capillary column. Condition as per manufacturer's directions.

Column 2 — 30 m x 0.32 mm fused silica (1 um film thickness) DB-5 wide-bore capillary column. Condition as per manufacturer's directions.

Column 3 — 0 m x 0.32 m fused silica (1 um film thickness) DB-17 wide-bore capillary column. Condition as per manufacturer's directions.

Column 4 — Supelcoport (100/120 mesh) coated with 1.5% SP-2250/ 1.95% SP-2401 packed in a 1.8 m x 4 mm I.D. glass column.

5.2 DATA SYSTEM

The AQUARIUS (HP-RTE A) and ENVIROQUANT (PC) data system is capable of quantitation using multipoint calibration.

5.3 SYRINGES

5.3.1 10 ul graduated, manually held (Hamilton or equiv.).

5.3.2 10 ul graduated, autosampler (Hamilton or equiv.).

6.0 REAGENTS AND STANDARDS

6.1 Solvents - Ultra pure, chromatography grade Hexane.

6.2 Stock standard solutions.

6.2.1 Commercially prepared standards used.

Supelco (or equivalent):	
Pesticides mix.	(2000 ug/ml)
Toxaphene	(200 ug/ml)
Chlordane	(200 ug/ml)
AR-1016	(200 ug/ml)
AR-1221	(200 ug/ml)
AR-1232	(200 ug/ml)
AR-1242	(200 ug/ml)
AR-1248	(200 ug/ml)
AR-1254	(200 ug/ml)
AR-1260	(200 ug/ml)

Accustandard (or equivalent):
Pesticide spike standard (M-001H)

6.2.2 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

6.3 Calibration standards.

6.3.1 Calibration standards are prepared at a minimum of the following five concentration levels, including surrogates, from the stock standards.

Pesticide (16 single component mixture):
5, 10, 25, 50, 75 and 100 ug/l

Methoxychlor:
25, 50, 125, 250, 375 and 500 ug/l

Toxaphene:
500, 1000, 1500, 2000 and 3000 ug/l

Chlordane:
50, 100, 500, 750 and 1000 ug/l

PCBs:
80, 200, 500, 1000, 3000 ug/l

6.3.2 See the Pesticide Standard Logbook for preparation of working standards.

6.4 *Surrogate spike solution.*

The surrogate solution is prepared as listed below, in Acetone at 1 ug/ml.

6.4.1 Take 1 ml surrogate stock solution (section 6.2.1) into 100 ml volumetric flask and adjust to 100 ml with Acetone. This standard is given to extraction to add 1 ml per sample aliquot or 1 ug/sample aliquot. Refer to 10.5 for calculations.

6.5 *Matrix spike solution.*

6.5.1 The pesticide matrix spike solution is prepared in Acetone at varying concentrations depending on the compound at 0.25 ug/ml (Refer to the Pest Std. Logbook).

6.5.2 The PCBs matrix spike solution is prepared in Acetone at 2 ug/ml (Refer to Pest Std Logbook).

6.6 *Breakdown evaluation solution.*

The DDT and Endrin breakdown evaluation solution is prepared in hexane at 100 and 250 ug/l, respectively. (Refer to the Pest Std. Logbook).

7.0 CALIBRATION

7.1 The calibration ranges are shown in section 6.3.1.

7.2 The linear range covered by this calibration is highest concentration standard.

7.3 Aliquot proper amount of each calibration standard into a crimp top vial.

7.4 The Calibration Factor (CF) is defined in section 11.1.

7.5 Initial calibration.

The percent relative standard deviation (% RSD) (see section 11.2) must be less than 20 % for each analyte of interest.

7.6 Continuing calibration (CBCHK).

7.6.1 A Continuing calibration check standard at mid-level concentration must be acquired every 10 samples.

7.6.2 The percent difference(%D)(see section 11.3) must be less than 15 for each compound of interest.

7.6.3 If %D criteria is met, the continuing calibration is considered valid.

7.6.4 If %D criteria fail, a new five point calibration must be performed.

8.0 RETENTION TIME WINDOWS

8.1 Retention time windows must be calculated for each analyte on each GC column and whenever a new GC column is installed. The data must be retained in the laboratory.

8.2 Make three injections of all single component standard mixture and multi-response products at approximately equal intervals during the 72-hr period.

8.3 Calculate the standard deviation of the three absolute retention times for each single component pesticide.

8.4 For multi-response pesticides or PCBs, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in the samples.

8.5 Apply plus or minus three times the standard deviations to retention time of each pesticide/PCB standard (continuing calibration or middle level of initial calibration). This will be used to define the retention time window for the sample.

8.6 In those cases where the retention time window for a particular pesticide/PCB is less than .01 minutes, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

9. PROCEDURE

9.1 Instrument conditions.

Recommended instrument conditions are listed in Table 1. Modifications are allowed as long as criteria of calibration are met.

9.2 Sample preparation.

Refer to SOPs GCP006 and/or GCP009.

9.3 Sample cleanup.

The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements.

9.3.1 If the sample contains high molecular weight materials, the use of GPC cleanup (Method 3640) is recommended.

9.3.2 If only PCBs to be analyzed in the sample, the use of sulfuric acid cleanup is recommended.

9.3.3 If both PCBs and pesticides to be analyzed in the sample, the use of florisil cleanup is recommended.

9.4 The GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated the mid-level standard. Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day.

9.5 DDT and Endrin breakdown evaluation .

9.5.1 Before running the first pesticide calibration standard analysis of the sequence, inject 2 ul of an evaluation standard directly on column. (Refer to Pest. Std. Logbook).

9.5.2 Calculate the percent breakdown for Endrin and DDT. (See section 11.7)

9.5.3 If degradation of either DDT or Endrin exceeds 20 %, take corrective action before proceeding with calibration.

9.5.4 Refer to SOP GCP098.SOP for GC system maintenance outline.

9.6 Daily calibration check.

See section 7.6.

9.7 Sample analysis (Primary).

9.7.1 The external standard technique is performed.

9.7.2 Inject 2 ul of the sample extract.

9.7.3 If one or more compounds have a response greater than full scale of highest standard, the extract requires dilution.

9.7.4 A mid-concentration standard must also be injected at intervals of 10 samples and at the end of the analysis sequence for CLP methodologies.

9.7.5 When the extracts are not being used for the analyses, store them at 4^0 C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

9.8 Sample analysis (Confirmatory).

9.8.1 Confirmation analysis is to confirm the presence of all compounds tentatively identified in the primary analysis.

9.8.2 Confirmation analysis is performed by using the different GC column from primary analysis.

9.8.3 The only standards that are required are the evaluation standard and standards of all compounds to be confirmed.

9.8.4 Quantitation may be performed on the confirmation analysis when standards meet the calibration criteria.

9.9 Data interpretation.

9.9.1 Qualitative identification.

The targeted compounds shall be identified by analyst with competent knowledge interpreting retention time and/or chromatographic pattern by comparison of the sample to the standard of the suspected compound. The criteria required for a positive identification are:

9.9.1.1 The sample component must elute at the daily absolute retention time window (Refer to section 8.5 and 8.6) for both primary and confirmation run.

9.9.1.2 For multi-response pesticides or PCBs, the GC pattern in the samples should resemble the pattern in the identified standard. Be aware of matrix interfering effects on peak shape and relative peak ratios which could distort the pattern. Interpretation of this phenomena may require a highly experienced chromatographic analyst or a second opinion.

9.9.2 Quantitative analysis.

9.9.2.1 When a target compound has been identified, concentration (see section 10.4) will be based on the integrated area or height of the peak and calculated by external standard technique.

9.9.2.2 For multi-response pesticides or PCBs, concentration will be calculated from the average of three to five non-interfered major peaks.

10. QUALITY CONTROL

QC Requirements Summary.

Calibration Check std.	Every 10 samples
Batch blank	one per analytical batch* or per extraction batch
Matrix Spike	one per analytical batch*
Matrix Spike Duplicate	one per analytical batch*
Blank Spike	one per analytical batch*
Surrogate	every sample and standard

* A batch is defined as a maximum of twenty samples, an SDG or once a month, whichever is more frequent.

10.1 Breakdown evaluation - refer to section 9.5.

10.2 Daily calibration check - refer to section 7.6.

10.3 Method blank.

10.3.1 The method blank should be carried through all stages of the sample preparation and measurement.

10.3.2 An acceptable method blank must be analyzed once for each extraction batch.

10.3.3 No compound can be present above the RDL. See Tables 3 & 3A for RDLs.

10.3.4 Recovery of the surrogates should fall within the QC criteria. See Table 2.

Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 3SP.

10.3.5 If the method blank does not meet surrogate criteria and/or target compounds are detected above RDLs, the entire batch must be re-extracted.

10.4 Matrix Spike (MS)/Matrix Spike Duplicate (MSD)/Blank spike

10.4.1 One sample from each analytical batch is selected and spiked in duplicate with select compounds to check precision and reproducibility.

10.4.2 Matrix spikes are prepared by spiking an actual sample at a concentration of 40/80/240 ug/l for pesticides and 200 ug/l for Aroclor-1016 and Aroclor-1260.

10.4.3 Percent recoveries (% R) (see section 11.5) are compared to the acceptance criteria listed in Table 4.

Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 2SP.

10.4.4 A relative percent deviation (RPD) (see section 11.6) is calculated and compared to RPD criteria in Table 4 .

10.4.5 If matrix spike recoveries do not meet the criteria (see Table 4) and the QC check sample (QCCS - blank spike) does meet the criteria, matrix interference is to be assumed and the data is reportable.

10.4.6 If QCCS (blank spike) does not meet the criteria, the batch should be re-extracted or the data should be qualified.

10.5 Surrogate.

10.5.1 All blanks, samples, and matrix spikes contain surrogate compounds which are used to monitor performance of the extraction, cleanup (when used), and analytical system.

10.5.2 Two surrogate standards, Tetrachloro-m-xylene (TCMX) and Decachlrobiphenyl (DCB), are added to each sample; however, only one needs be calculated for recovery.

10.5.3 If the recovery (refer to 11.5) of both surrogate compounds do not meet the QC criteria (see Table 2), the following must be done:

10.5.3.1 All calculations must be checked, if no problem is detected then reanalyze the sample.

10.5.3.2 Re-extract if no problem is detected and reanalysis yields the same results.

Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 3SP.

10.5.4 The retention time shift for surrogate must be evaluated after the analysis of each sample.

10.5.5 The sample must be reanalyzed when the retention time for both surrogates is out of control limit.

10.5.6 The above conditions (section 10.5.4) are not required for samples having visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. This judgment should be approved by team leader or supervisor.

11. CALCULATION

11.1 Calibration Factor (CF).

$$CF = \frac{As}{Cs}$$

where: As = Area of the peak for the compound being measured.
Cs = Concentration of the compound being measured (ug/l).

11.2 Percent Relative Standard Deviation (% RSD).

$$\% RSD = \frac{SD}{CFav} \times 100$$

where: SD = Standard Deviation.
CFav = Average calibration factor from initial calibration.

11.3 Percent Difference (% D).

$$\% D = \frac{|CFav - CFc|}{CFav} \times 100$$

where: CFc = CF from continuing calibration (CBCHK).

11.4 Concentration (Conc.).

For water:

$$Conc.\ (ug/l) = \frac{Ac \times Vf \times D}{CFav \times Vi}$$

For soil/sediment (on a dry weight basis):

$$Conc.\ (ug/Kg) = \frac{Ac \times Vf \times D}{CFav \times Ws \times M}$$

where: Ac = Area of peak for compound being measured.
Vf = Final Volume of total extract (ml).
D = Secondary dilution factor.
Vi = Initial volume of water extracted (ml).
Ws = Weight of sample extracted (g).
M = (100 - % moisture in sample) / 100
or % solid/100.

11.5 Percent Recovery (% R).

$$\%\ R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

11.6 Relative Percent Difference (RPD).

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

where: MSC = Matrix Spike Concentration.
MSDC = Matrix Spike Duplicate Concentration.

11.7 Percent Breakdown.

$$\%\ \text{breakdown for DDT} = \frac{\text{Total DDT degradation peak area}}{\text{Total DDT peak area}} \times 100$$

where: Total DDT degradation peak area = DDE + DDD
Total DDT peak area = DDT + DDE + DDD

$$\%\ \text{breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area}}{\text{Total Endrin peak area}} \times 100$$

where: Total Endrin degradation peak area = Endrin aldehyde + Endrin ketone.
Total Endrin peak area = Endrin + Endrin aldehyde + Endrin ketone.

12.0 Documentation

12.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

12.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log.

12.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

12.2.1 The Accutest Lot Number and expiration date must be cross reference on the standard vial.

12.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

Table 1

Recommended Operating Conditions

Item	Condition
Carrier Gas	Helium
	5% Methane / 95% Argon
Makeup Gas	5% Methane / 95% Argon
Makeup gas flow	approx. 30 ml/min
Injection port temp.	210-225 oC
Capillary Column:	
Injection type	Splitless
Purge off time	0.8 min
Column Flow	5 - 8 ml/min
Septum purge flow	1 ml / min
Initial Temperature	160oC
Time 1	0.5 min
Column Temp. rate	5oC / min
Final Temperature	250 - 320oC (based on column type)
Packed Column:	
Column flow	30ml / min
Temperature program	Isothermal @ 190 -200oC

Table 2

Surrogate Criteria

Surrogate	QC Limits 1 :	QC Limits:	QC Limits:
		water	soil
	%	%	%
Decachlorophenyl	60-150	32-149	37-161
Tetrachloro-m-xylene	60-150	27-169	36-142

(1) Default Limits. Use these limits until advised by the Manager.

Table 3

Matrix: Soil

Compound (1)	RDL (2)
Aldrin	0.095
alpha-BHC	0.021
beta-BHC	0.03
delta-BHC	0.037
gamma-BHC (lindane)	0.022
Chlordane	0.06
alpha-Chlordane	0.022
gamma-Chlordane	0.025
Dieldrin	0.026
4,4'-DDD	0.054
2,4-DDD	0.05
4,4'-DDE	0.026
2,4'-DDE	0.05
4,4'-DDT	0.12
2,4'-DDE	0.05
Endrin	0.043
Endosulfan Sulfate	0.11
Endrin Aldehyde	0.04
Endrin Ketone	0.2
Endosulfan-I	0.027
Endosulfan-II	0.034
Heptachlor	0.026
Heptachlor Epoxide	0.027
Methoxychlor	0.022
Toxaphene	2
Arochlor - 1016	0.53
Arochlor - 1221	0.19
Arochlor - 1232	0.42
Arochlor - 1242	0.29
Arochlor - 1248	0.22
Arochlor - 1254	0.33
Arochlor - 1260	0.46

All values expressed in ug/kg

Table 3A

Matrix: Water

Compound (1)	RDL (2)
Aldrin	0.022
alpha-BHC	0.015
beta-BHC	0.019
delta-BHC	0.016
gamma-BHC (lindane)	0.017
Chlordane	0.22
alpha-Chlordane	0.022
gamma-Chlordane	0.02
Dieldrin	0.021
4,4'-DDD	0.033
2,4-DDD	0.05
4,4'-DDE	0.023
2,4'-DDE	0.05
4,4'-DDT	0.025
2,4'-DDE	0.05
Endrin	0.027
Endosulfan Sulfate	0.046
Endrin Aldehyde	0.032
Endrin Ketone	0.03
Endosulfan-I	0.023
Endosulfan-II	0.024
Heptachlor	0.018
Heptachlor Epoxide	0.021
Methoxychlor	0.022
Toxaphene	0.28
Arochlor - 1016	0.23
Arochlor - 1221	0.19
Arochlor - 1232	0.054
Arochlor - 1242	0.025
Arochlor - 1248	0.4
Arochlor - 1254	0.2
Arochlor - 1260	0.31

All values expressed in ug/l.

Table 4

Water

Compound	Default QC limits * :		QC Limits:		
	MS-MSD-BSP	RPD	MS-MSD	BSP	RPD (1)
	%	%	%	%	%
Aldrin	50-150	30	81-118	85-119	--
alpha-BHC	50-150	30	79-129	84-132	--
beta-BHC	50-150	30	66-154	73-161	--
delta-BHC	50-150	30	76-127	81-119	--
gamma-BHC (lindane)	50-150	30	80-153	91-130	--
Chlordane	50-150	30	Default	Default	--
alpha-Chlordane	50-150	30	67-113	73-107	--
gamma-Chlordane	50-150	30	69-115	77-111	--
Dieldrin	50-150	30	88-128	84-128	--
4,4'-DDD	50-150	30	74-142	78-142	--
2,4-DDD	50-150	30	NA	NA	--
4,4'-DDE	50-150	30	67-128	82-131	--
2,4'-DDE	50-150	30	NA	NA	--
4,4'-DDT	50-150	30	48-134	75-132	--
2,4'-DDE	50-150	30	NA	NA	--
Endrin	50-150	30	77-140	82-128	--
Endosulfan Sulfate	50-150	30	86-132	88-135	--
Endrin Aldehyde	50-150	30	56-117	65-128	--
Endrin Ketone	50-150	30	88-100	Default	--
Endosulfan-I	50-150	30	12-102	16-103	--
Endosulfan-II	50-150	30	Default	Default	--
Heptachlor	50-150	30	62-169	77-146	--
Heptachlor Epoxide	50-150	30	63-172	82-149	--
Methoxychlor	50-150	30	50-148	42-172	--
Toxaphene	50-150	30	Default	Default	--
Arochlor - 1016	50-150	30	71-116	24-156	--
Arochlor - 1221	50-150	30	NA	NA	--
Arochlor - 1232	50-150	30	NA	NA	--
Arochlor - 1242	50-150	30	NA	NA	--
Arochlor - 1248	50-150	30	NA	NA	--
Arochlor - 1254	50-150	30	NA	NA	--
Arochlor - 1260	50-150	30	64-114	23-151	--

(*) Use default values until advised by the department manager.
(1) Insufficient data points, use default values.

Soil

Compound	Default QC limits * :		QC Limits:		
	MS-MSD-BSP	RPD	MS-MSD	BSP	RPD (1)
	%	%	%	%	%
Aldrin	50-150	30	62-127	69-118	--
alpha-BHC	50-150	30	60-133	73-113	--
beta-BHC	50-150	30	67-132	72-114	--
delta-BHC	50-150	30	58-132	69-117	--
gamma-BHC (lindane)	50-150	30	66-129	75-118	--
Chlordane	50-150	30	Default	Default	--
alpha-Chlordane	50-150	30	68-127	69-119	--
gamma-Chlordane	50-150	30	57-138	75-118	--
Dieldrin	50-150	30	76-146	71-121	--
4,4'-DDD	50-150	30	65-140	76-122	--
2,4-DDD	50-150	30	NA	NA	--
4,4'-DDE	50-150	30	59-138	70-121	--
2,4'-DDE	50-150	30	NA	NA	--
4,4'-DDT	50-150	30	53-149	59-135	--
2,4'-DDE	50-150	30	NA	NA	--
Endrin	50-150	30	69-129	66-131	--
Endosulfan Sulfate	50-150	30	60-150	75-125	--
Endrin Aldehyde	50-150	30	56-132	54-116	--
Endrin Ketone	50-150	30	63-119	70-116	--
Endosulfan-I	50-150	30	59-126	71-119	--
Endosulfan-II	50-150	30	55-121	71-118	--
Heptachlor	50-150	30	70-140	75-115	--
Heptachlor Epoxide	50-150	30	74-134	72-120	--
Methoxychlor	50-150	30	64-153	57-136	--
Toxaphene	50-150	30	Default	Default	--
Arochlor - 1016	50-150	30	70-128	66-122	--
Arochlor - 1221	50-150	30	NA	NA	--
Arochlor - 1232	50-150	30	NA	NA	--
Arochlor - 1242	50-150	30	NA	NA	--
Arochlor - 1248	50-150	30	NA	NA	--
Arochlor - 1254	50-150	30	NA	NA	--
Arochlor - 1260	50-150	30	66-130	60-117	--

(*) Use default values until advised by the department manager.
(1) Insufficient data points, use default values.

THIS LIST IS INCLUDED TO DEMONSTRATE ACCUTEST'S ROUTINE PESTICIDE REPORTING LIST.

Method Blank Summary

Job Number: E14806
Account: PENNONI Pennoni Associates Inc.
Project: John Sexton Co., 480 Pattison, Philadelphia, PA

Sample	File ID	DF	Analyzed	By	Prep Date	Prep Batch	Analytical Batch
OP1457-MB1	CD14099.D	1	09/25/96	LUN	09/24/96	OP1457	GCD719

The QC reported here applies to the following samples: **Method:** SW846 8080

E14806-1, E14806-2

CAS No.	Compound	Result	RDL	Units	Q
309-00-2	Aldrin	ND	0.095	ug/kg	
319-84-6	alpha-BHC	ND	0.021	ug/kg	
319-85-7	beta-BHC	ND	0.030	ug/kg	
319-86-8	delta-BHC	ND	0.037	ug/kg	
58-89-9	gamma-BHC (Lindane)	ND	0.022	ug/kg	
12789-03-6	Chlordane	ND	0.060	ug/kg	
60-57-1	Dieldrin	ND	0.026	ug/kg	
72-54-8	4,4'-DDD	ND	0.054	ug/kg	
72-55-9	4,4'-DDE	ND	0.026	ug/kg	
50-29-3	4,4'-DDT	ND	0.12	ug/kg	
72-20-8	Endrin	ND	0.043	ug/kg	
1031-07-8	Endosulfan sulfate	ND	0.11	ug/kg	
7421-93-4	Endrin aldehyde	ND	0.040	ug/kg	
959-98-8	Endosulfan-I	ND	0.027	ug/kg	
33213-65-9	Endosulfan-II	ND	0.034	ug/kg	
76-44-8	Heptachlor	ND	0.026	ug/kg	
1024-57-3	Heptachlor epoxide	ND	0.027	ug/kg	
72-43-5	Methoxychlor	ND	0.18	ug/kg	
8001-35-2	Toxaphene	ND	2.0	ug/kg	

CAS No.	Surrogate Recoveries		Limits
877-09-8	Tetrachloro-m-xylene	100%	60-150% [a]
2051-24-3	Decachlorobiphenyl	100%	60-150% [a]

(a) Advisory QC Limits.

THIS LIST IS INCLUDED TO DEMONSTRATE ACCUTEST'S ROUTINE PCB REPORTING LIST.

Blank Spike Summary

Job Number: E14064
Account: HANDNJ Handex Corporation
Project: Delaware Petroleum, Route 130 & Salem Street, Burlington, NJ

Sample	File ID	DF	Analyzed	By	Prep Date	Prep Batch	Analytical Batch
OP1387-BS2	CD13543.D	1	08/20/96	LUN	08/19/96	OP1387	GCD700

The QC reported here applies to the following samples: **Method:** ~~EPA 608~~ SW846 - 8080 MR.

E14064-2, E14064-8

CAS No.	Compound	Spike ug/l	BSP ug/l	BSP %	Limits
12674-11-2	Aroclor 1016	2	2.4	120	50-150
11104-28-2	Aroclor 1221		ND		50-150
11141-16-5	Aroclor 1232		ND		50-150
53469-21-9	Aroclor 1242		ND		50-150
12672-29-6	Aroclor 1248		ND		50-150
11097-69-1	Aroclor 1254		ND		50-150
11096-82-5	Aroclor 1260	2	2.4	120	50-150

CAS No.	Surrogate Recoveries	BSP	Limits
877-09-8	Tetrachloro-m-xylene	110%	60-150% [a]
2051-24-3	Decachlorobiphenyl	95%	60-150% [a]

(a) Advisory QC Limits.

Rev. Date: 12/05/95
F/N AAP073.SOP
Lab. Manager:
QA Manager:

TEST NAME: DIGESTION OF SOILS FOR FLAME AND ICP ANALYSIS AND DIGESTIONS OF SOILS FOR FURNACE ANALYSIS OF SB.

LAB AREA: AA

TEST CODES: All samples are updated to SCH in the metals prep department under the code of the metal to be analyzed.

DETECTION LIMIT: Not applicable.

1.0 SCOPE AND APPLICATION

This method is applicable for the digestion of sediments, soils, sludges, and solids wastes. After digestion, the samples can be analyzed by ICAP or by flame AAS. This digestion method is based upon SW846 method 3050A.

2.0 PRESERVATION

Non-aqueous samples should be refrigerated at the time of receipt.

3.0 HOLDING TIME

All samples should be digested and analyzed within 6 months of the time of collection.

4.0 INTERFERENCES

Sludge and soil samples can contain diverse matrix types which may contain a variety of interferences. Spiked samples can be used to determine if these interferences are adequately treated in the digestion process. For a discussion of other interferences, refer to specific analytical methods.

5.0 APPARATUS

The apparatus needed for this digestion procedure are listed below. It should be noted that hot plates and beakers with watch glasses may be used in place of the digestion block and digestion tubes.

5.1 Digestion block. Designed to hold sample digestion tubes and capable of temperature control.

5.2 Sample digestion tubes. 120 ml Pyrex glass tubes.

5.3 Automatic pipeter bottles.

5.4 100 ml volumetric flasks.

5.5 Glass funnels.

5.6 Whatman #41 filter paper or equivalent.

5.7 Top loader balance.

6.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required.

6.1 Hydrochloric acid. Baker instra-analyzed or equivalent.

6.2 Nitric Acid. Baker instra-analyzed or equivalent.

6.3 Hydrogen Peroxide, 30 %.

6.4 Metals Spiking Solutions. All metals spiking solutions should be made up in a solution of 2 % nitric acid following the procedures outlined in the metals standards preparation SOP.

7.0 PROCEDURE

7.1 Weigh out 1 to 2 g of sample into a numbered digestion tube or a beaker. If the sample has a low percent solids, a larger sample size may be used to obtain a weight

approximately equivalent to 1 g of dry sample. The sample should be weighed out using a top loader balance and the weights should be recorded to two places past the decimal. Make sure that the sample has been thoroughly mixed before weighing out the representative sample. Discard rocks, sticks, etc. from the sample. Make sure that the sample identification is accurately recorded with the digestion tube/beaker numbers on the sample digestion log. In addition to the samples, a Spike Blank or a Lab Control and a Method Blank should be set up with each batch of 20 samples or less. A Matrix Spike and a Duplicate (or matrix spike duplicate) should be set up with each batch of 20 samples. Check with the metals supervisor for spiking levels to use for the matrix spike and the spike blank or lab control.

7.2 Add 10 ml of 1:1 nitric acid to all quality control and samples.

7.3 Place the numbered tubes into a digestion block. (If using beakers, cover the beakers with watch glasses and place them on a hot plate.) Heat the samples until they come to a gentle reflux and then continue to heat the samples for an additional 10 to 15 minutes. Do not allow the samples to boil. After the heating is complete, allow the samples to cool.

7.4 Add an additional 5 ml of concentrated nitric acid to all Quality Control and samples. Heat the samples at a gentle reflux for an additional 30 minutes. Do not allow the volume to be reduced to below 5 ml. Cool.

7.5 Add 2 ml of water and 3 ml of 30 % hydrogen peroxide to each sample and reflux until effervescence subsides. Cool.

7.6 Continue to add 30 % hydrogen peroxide in 1 ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 ml of 30 % hydrogen peroxide.

7.7 Add 5 ml of 1:1 HCl and 10 ml of water and reflux for an additional 15 minutes.

7.8 Filter the samples through Whatman #41 filter paper into 100 ml volumetric flasks. Make sure to rinse the digestion tubes and the filter paper well with distilled, deionized water. Dilute to volume with distilled, deionized water. The samples are now ready for analysis by ICAP or flame AAS.

8.0 QC REQUIREMENTS

8.1 For each digestion batch of 20 samples or less, a Spike Blank (or a lab control) and a Method Blank should be prepared.

8.2 For every 20 samples, a matrix spike and a duplicate (or matrix spike duplicate) should be prepared.

8.3 Refer to the analytical methods SOPs for additional information on method quality control.

9.0 GLASSWARE CLEANING

9.1 All glassware should be washed with soap and tap water and then soaked in a 5% nitric acid bath for several hours. It should then be rinsed at least 3 times with distilled, deionized water.

10.0 DOCUMENTATION REQUIREMENTS

10.1 All digestion information should be entered on a digestion log. The information required includes the sample identification, the initial sample volume, the final sample volume, the acids used (including both amount and lot number), the spikes used, and the digestion times.

10.2 The analyst should write additional information such as unusual sample characteristics in the comments section. All spiking solution information should be entered in the metals spiking solution notebook. Refer to the standards SOP for additional information on documentation requirements to follow when making spiking solutions.

11.0 SAFETY

The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

Rev. Date: 11/04/96
F/N AAP070.SOP
Lab. Manager: [signature]
QA Manager: [signature]

TEST NAME: DIGESTION OF NON-POTABLE WATERS FOR ICP AND FLAME ANALYSIS.

LAB AREA: AA

TEST CODES: All samples are updated to SCH in the metals prep department under the code of the metal to be analyzed.

DETECTION LIMIT: Not applicable.

1.0 SCOPE AND APPLICATION

This method is applicable for the digestion of aqueous samples, TCLP extracts, and wastes that contain small amounts of suspended solids. After digestion, the samples can be analyzed by ICP or by flame AAS. This digestion method is based on SW846 3010A and the EPA water digestion method in method 200.7 from "Methods for Chemical Analysis of Water and Wastes", March 1983.

2.0 PRESERVATION

All samples should be preserved with nitric acid at the time of collection.

3.0 HOLDING TIME

All samples should be digested and analyzed within 6 months of the time of collection.

4.0 INTERFERENCES

Organics in a matrix may cause interferences if the sample is not digested rigorously enough. In addition, high levels of acids in the final digestate may cause interferences in the analysis. Both of these interferences can be avoided by choosing the appropriate digestion method and by bringing the sample to an appropriate final volume. For a discussion of other interferences, refer to specific analytical methods.

5.0 APPARATUS

The apparatus needed for this digestion procedure are listed below. It should be noted that hot plates and beakers with watch glasses may be used in place of the digestion block and digestion tubes.

5.1 Digestion block. Designed to hold sample digestion tubes and capable of temperature control.

5.2 Sample digestion tubes. 120 ml Pyrex glass tubes.

5.3 Automatic pipeter bottles.

5.4 50 ml volumetric flasks.

5.5 Glass funnels.

5.6 Whatman #41 filter paper or equivalent.

6.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required.

6.1 Hydrochloric acid. Baker instra-analyzed or equivalent.

6.2 Nitric Acid. Baker instra-analyzed or equivalent.

6.3 Metals Spiking Solutions. All metals spiking solutions should be made up in a solution of 2 % nitric acid following the procedures outlined in the metals standards preparation SOP.

7.0 PROCEDURE

Below is the procedure to be followed for the digestion of aqueous samples prior to ICP or flame AAS analysis.

7.1 Measure out 50 ml of each sample into a labeled digestion tube or into a beaker. The sample may be measured by using a graduated cylinder or by using a calibrated digestion tube. Make sure that the sample identification is accurately recorded with the digestion tube/beaker numbers on the sample digestion log. In addition to the samples, a Spike Blank or a Lab Control and a Method Blank should be set up with each batch of 20 samples or less. A Matrix Spike and a Duplicate (or matrix spike duplicate) should be set up with each batch of 20 samples. Check with the metals supervisor for spiking levels to use for the matrix spike and the spike blank or lab control.

7.2 Add 1.5 ml of concentrated nitric acid to all quality control and samples.

7.3 Place the labeled tubes into a digestion block. (If using beakers, cover the beakers with watch glasses and place them on a hot plate.) Heat the samples until they come to a gentle reflux and then continue to heat the samples for approximately 2 hours to reduce the volume. After the heating is complete, allow the samples to cool.

7.4 Add an additional 1.5 ml of concentrated nitric acid to all quality control and samples. Continue heating the samples at a gentle reflux until the sample is completely digested. (More acid may be added as necessary to complete the digestion.)

7.4.1 If the digestion appears to be complete at the end of step 7.3, then step 7.4 may be omitted.

7.4.2 Signs of a complete digestion are if the digestate is light in color and/or if the appearance of the sample does not changes with continued refluxing.

7.5 Add 5 ml of 1:1 HCl to each sample and reflux for an additional 15 minutes.

7.6 Bring the sample to a final volume of 50 ml with distilled, deionized water. If the sample contains particulate, it can be filtered through Whatman # 41 filter paper (or equivalent) before analysis. The sample is now ready for analysis by ICP or flame AAS.

8.0 QC REQUIREMENTS

8.1 For each digestion batch of 20 samples or less, a Spike Blank (or a lab control) and a Method Blank should be prepared.

8.2 For every 20 samples, a matrix spike and a duplicate (or matrix spike duplicate) should be prepared.

8.3 Refer to the analytical methods SOPs for additional information on method quality control.

9.0 GLASSWARE CLEANING

9.1 All glassware should be washed with soap and tap water and then soaked in a 5% nitric acid bath for several hours. It should then be rinsed at least 3 times with distilled, deionized water.

10.0 DOCUMENTATION REQUIREMENTS

10.1 All digestion information should be entered on a digestion log. The information required includes the sample identification, the initial sample volume, the final sample volume, the acids used (including both amount and lot number), the spikes used, and the digestion times.

10.2 The analyst should write additional information such as unusual sample characteristics in the comments section. All spiking solution information should be entered in the metals spiking solution notebook. Refer to the standards SOP for additional information on documentation requirements to follow when making spiking solutions.

11.0 SAFETY

The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

Rev. Date: 12/06/95
File: AAP203.SOP

Lab Manager: M F Cole
QA Manager:

TEST NAME: **METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICAP).**

LAB AREA: AA

METHOD REF: SW846 6010A

TEST CODES: A variety of metals can be analyzed by ICAP. These include Ba, Be, Cd, Cr, Co, Cu, Mn, Mo, Ni, Ag, V, Zn, Al, Ca, Fe, Mg, K, Na. Lower detection limits can be obtained for metals such as As, Pb, Sb, Tl, and Se using the Trace ICP.

REPORTING LIMITS: Reporting limits are approximately based on the PQL's for each metal. Refer to table 1 for current standard reporting limits.

1.0 SCOPE AND APPLICATION

This method is applicable for the determination of metals in water, sludges, sediments, soils. Sample matrices are pretreated following SW846 methods for digestion of soil, sediment, sludge or water samples. Refer to specific digestion SOP's for more information on digestion techniques.

2.0 PRESERVATION

All water samples should be preserved with nitric acid to a pH of less than 2. All samples should be stored in a refrigerator at 4°C before digestion.

3.0 HOLDING TIME

All samples should be analyzed within 6 months of the date of collection.

4.0 INTERFERENCES

Several types of interferences can cause inaccuracies in trace metals determinations by ICP. These interferences are discussed below.

4.1 Spectral interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. Corrections for these interferences can be made by using interfering element corrections, by choosing an alternate analytical line, and/or by applying background correction points.

4.2 Physical interferences can be caused by changes in sample viscosity or surface tension, by high acid content in a sample, or by high dissolved solids in a sample. These interferences can be reduced by making sample dilutions or by analyzing a sample using the method of standard additions.

4.3 Chemical interferences are not pronounced with ICAP due to the high temperature of the plasma, however if they are present, they can be reduced by optimizing the analytical conditions (i.e. power level, torch height, etc.).

5.0 APPARATUS

Currently there are two ICAPs available for use in the lab, a Thermo Jarrell Ash 61E and a Thermo Jarrell Ash Trace ICP. Both units are simultaneous units. The Trace unit has been optimized to obtain lower detection limits for arsenic, selenium, antimony, lead, and thallium. This optimization was done using a horizontal torch, a vacuum optics system, optimized photomultiplier tubes, and Crawford-Kunselman Noise Reduction techniques. The lines programmed into the 61E system are shown in Table 2A. The lines programmed into the Trace system are shown in Table 2B. Additional elements and lines may be analyzed using an off-peak analysis function.

6.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water must be used whenever water is required.

6.1 Hydrochloric acid, trace metals grade.

6.2 Nitric Acid, Baker instra-analyzed or equivalent.

6.3 Standard stock solutions available from Inorganic Ventures, Spex, Plasma Pure or equivalent. Note: All standards must be ICP quality standards.

6.4 Calibration Standards. These can be made up by diluting the stock solutions to the appropriate concentrations.

6.4.1 Standards should be approximately matrix matched to the samples. For most samples, a 3 percent nitric acid and 5 percent hydrochloric acid will approximate the acid matrix of the sample and limit nebulization problems. If it is known that the samples contain a significantly different acid matrix, then the matrix of the standards should be modified or the samples should be diluted so that they are in a similar matrix to the curve.

6.4.2 Standards should be prepared so that there is minimal spectral interference between analytes.

6.4.3 Refer to the standards book for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP. Suggested levels for the high standard are shown in Table 3. Unless otherwise approved, the calibration curve should consist of a blank and 3 standards.

6.5 Analytical Quality Control Solutions. All of the solutions below are prepared by adding either mixed or single element metals solutions to a solution containing 3 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture.

6.5.1 Initial Calibration Verification solution. This standard solution must be made from a different source than the calibration curve. The values for each element should be within the range of the calibration curve. This solution is used to verify the accuracy of the initial calibration.

6.5.2 Continuing Calibration Verification solution. The metals concentrations for this standard should be at approximately the mid-point of the calibration curve for each element. This standard should be prepared from a different source that than used for the calibration curve.

6.5.3 Interference Element Check Solutions. These solutions should be used on a periodic basis to check the interfering element corrections on the instruments. Note: If interferences from different elements than those listed below are a problem, the interfering

element solutions may be modified. (Note: the solutions outlined in the SOP for method EPA 200.7 are acceptable for this purpose.) Two acceptable solutions are outlined below.

6.5.3.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below.

Al	500 mg/L
Ca	500 mg/L
Fe	200 mg/L
Mg	500 mg/L

6.5.3.2 ICSAB Solution. The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below.

Ag	1.0 mg/L	Al	500 mg/L
Ba	0.50 mg/L	Ca	500 mg/L
Be	0.50 mg/L	Fe	200 mg/L
Cd	1.0 mg/L	Mg	500 mg/L
Co	0.50 mg/L		
Cr	0.50 mg/L		
Cu	0.50 mg/L		
Mn	0.50 mg/L		
Ni	1.0 mg/L		
Pb	1.0 mg/L		
V	0.50 mg/L		
Zn	1.0 mg/L		

6.5.4 CRI Standards (Optional). The CRI standards contain the elements of interest at levels near the low end of the curve. Refer to the CLP SOP for additional details. Note: This QC check is optional for this method.

6.6 Matrix Spike and Lab Control Solution. The metals should be at the final concentrations shown in Table 4. This solution is prepared by adding either mixed or single element metals solutions to a solution containing 3 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. Two mls of this stock solution should be added to the lab control and the matrix spike before they are digested and brought to a final volume of 100 ml.

6.7 Liquid Argon or Argon Gas. Cylinders are provided by Air Products and are supplied to the metals lab from the tank distribution room. See metals supervisor for proper gas access.

6.8 Yttrium Internal Standard. For the TJA Trace, a yttrium internal standard may be used. Check with the lab supervisor for additional information on using this standard.

7.0 PROCEDURE

General procedures on how to operate the TJA 61E and the Trace are described below. The ThermoSpec software is used to run both instruments and it can be accessed either in a Windows environment or from a DOS environment. Note: When leaving most menus in the ThermoSpec software, an F9 command is required to save the changes. In order to avoid losing information, make sure that you exit screens by first using this Done/Keep command (F9).

7.1 Before bringing up the instrument, make sure that the lines, the nebulizer, and the spray chamber are clean and that there are no leaks in the torch area.

7.2 Slowly turn on the liquid argon and turn on the recirculating cooler.

7.3 Engage the peristaltic pump.

7.4 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.)

7.5 Enter the Thermospec software and go to the SETUP menu. Then move to the Plasma Control Panel option. Ignite the instrument by entering Start-up (F1) and then enter F9 to continue. After the plasma is ignited set the pump rate to 100 using the Levels option (F2).

7.6 Make sure that the sample tip is in the rinse solution and then let the instrument warm up for at least 30 minutes. If a yttrium internal standard is being used, make sure that sufficient solution is in place to last the length of the run and that the standard is being properly introduced into the sample introduction system. Check with the lab supervisor for additional details.

NOTE: While the instrument is warming up, the standards should be prepared and the samples that are to be analyzed should be collected together along with the required quality control.

7.7 After the instrument has warmed up, the nebulizer should be optimized. The procedures for both the TJA 61E and the TJA Trace are given below.

7.7.1 For the TJA 61E, go to the SETUP menu. The nebulizer can be optimized by running a 1000 ppm solution of Sodium or Yttrium. This should be done on a daily basis. For the sodium standard, the top of the yellow flame should be at the top of the torch. For the Yttrium standard, the tip of the red flame should be at the top of the torch. If it is not, change the nebulizer gas rate using the Levels option (F2) until the flame tip is in the proper position. Note: Make sure that this same nebulizer gas rate is entered into the analysis program that is to be used.

7.7.1.1 For the TJA 61E, it is recommended that the torch height optimization be checked whenever the torch is removed and replaced or whenever there is a decrease in sensitivity. This can be done using the following procedure. Aspirate a plasma solution containing 10 ug/ml each of As, Pb, Se, and Tl. Collect intensity data the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the top of the work coil. Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the largest intensity ratio for the least sensitive element of the four analytes. If more than one position provides the same ratio, select the position that provides the best compromise of intensity ratios of all four analytes.

7.7.2 For the TJA Trace, the nebulizer position and pressure should also be adjusted to achieve the highest signal to background ratio. To do this, go the method OPTNEB. Adjust the nebulizer pressure to the point between 25 and 35 PSI (normally approximately 28 psi) where the

intensity is highest in relation to the lowest rsd. Then physically adjust the glass nebulizer in the spray chamber by rotating it or moving it in and out until the highest intensity is obtained for the 10 ug/ml As standard.

7.7.2.1 For the TJA Trace, it is recommended that the torch placement optimization be checked whenever the torch is removed and replaced or whenever there is a decrease in sensitivity. This can be done using the following procedure. Aspirate a blank into the instrument and measure the intensity. Adjust the torch position using the manual thumb screws in the compartment to the left of the nebulizer compartment. The torch should be positioned to obtain the lowest intensity reading for the blank.

7.8 Next profile the instrument by aspirating a know concentration solution of an element. The element used for the profiling the instrument should be picked to minimize the element shifts for all of the elements in the method. Normally, the automatic profile program will properly profile the instrument. However, the manual profile program can be used if the instrument profile has drifted significantly. The profile can be done as an option from the SETUP menu or an option from the OPERATION menu.

7.9 Move to the DEVELOPMENT menu and go to the Methods option. Open the analytical program that you will be using and move to the MethodInfo option (F3). Type in the file name that will be used to save the run data next to the space marked Analysis Data File. The name should be in the form of instrument ID, date in the order month/date, matrix identifier, and run number. For example, the first mixed (water and soil) analysis on Dec. 1 on the TJA 61E would be designated T1201M1. The first mixed analysis on Dec. 1 on the TJA Trace would be designated R1201M1.

7.10 Move to the PlasmaInfo option under DEVELOPMENT and enter the auxiliary pump rate determined in 7.8 above.

7.11 Go to the OPERATION menu. If you are going to be running samples using the autosampler, then set up the autosampler table to be used for the analysis using the autosampler setup option. Make sure to reference the proper analysis program in the autosampler table. Also make sure to

include all dilutions factors for serial dilutions or other required dilutions in the autosampler table. Note: You can set up a new autosampler table for another run while your current run is going using Windows. When the software is properly set up, Alt/Tab will take you from Thermospec into Windows.

7.12 Calibrate the instrument. Unless otherwise approved, the calibration should consist of a blank and 3 standards. The calibration curve must have a correlation coefficient of greater than or equal to 0.995. This calibration criteria must be met before any samples can be analyzed. (Note: the calibration standards may be included in the autosampler program or they may be run separately.) Check with the area supervisor or manager for approval for an abbreviated curve.

7.13 As the instrument conditions shift, the instrument can be optimized by updating the calibration curve. This can be done either through the QC analyze function or using the normalization function in the autosampler table. The slope can be updated using the high calibration standard and the intercept can be updated using the calibration blank. Note: A slope or intercept update must always be surrounded by CCV, CCB check pairs that meet all QC criteria for any elements that are being reported.

7.14 After the instrument is properly calibrated, begin by reanalyzing the high standard(s) for each element. (Note: The standards can be combined into one solution for this analysis). The analyzed value must be within 5 percent of the true value or that element should be recalibrated. After the high standards are analyzed, analyze the ICV and ICB check standards. For the ICV, all elements to be reported must be within 10 percent of the true values. After the ICV and ICB and before any actual samples are analyzed, the CCV and CCB should be analyzed. For the CCV, all elements to be reported must be within 10 percent of the true values.

7.15 Before analyzing any real samples, the interfering element solutions must be checked. For all spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solutions should contain less than the reporting limit for each element. Note: The optional CRI check should be analyzed before the interfering element check solutions if it is to be analyzed. The interfering element solutions must also be checked at the end of the run or after a maximum of 8 hours.

7.16 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control should be analyzed. Each sample analysis should be a minimum of 3 readings using at least a 5 second integration time. Between each sample, flush the nebulizer and the solution uptake system with a blank rinse solution for 60 seconds or for the required period of time to ensure that analyte memory effects are not occurring.

7.17 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 10 percent of the true value, the CCV should be reanalyzed to confirm the initial value. If the CCV is not within 10 percent of the true value after the reanalysis, no samples can be reported in the area bracketed by the failing CCV. If the CCB is not less than the reporting limit for each element, then no samples can be reported in the area bracketed by the failing CCB.

7.18 For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution should be prepared. For the serial dilution, a 1:5 dilution should be made on the sample. The results of the 1:5 dilution should agree within 10 percent of the true value as long as the sample and the dilution result are greater than 10 times the method detection limit or greater than 50 times the IDL.

7.19 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample. A limit check table may be built into the autosampler file so that samples exceeding the linear range are flagged on the raw data.

7.20 After the run is completed, convert the data file to an ASCII format using the Enable program installed on the ICP computer. The data can be converted using the form EXTRACT.WPF. Save the converted file on a network drive (E:\metaldat\) using the file naming system described above, adding the designation I at the beginning of the file name to designate ICP. (Note: this procedure may be modified as changes are made to the lab network. See lab supervisor for further details.)

7.21 The data can be evaluated by running an automated data evaluation program which will help to generate quality control summary pages. Each run should be evaluated as quickly as possible to make sure that all required quality control has been analyzed.

7.22 At the end of the analysis day the ICAP must be brought down using the following sequence.

a) Rinse tip in a solution of 3% nitric acid, 5% HCl for 10 minutes and in DI water for 20 minutes. (Note: a stronger acid solution may be needed depending on the matrix of the samples that were analyzed.)
b) Turn off the plasma using the Plasma Control Option under the SETUP menu. F7 initiates the automatic shutdown procedure.
c) Release the tension on the pump tubing.
d) Turn off the cool flow and printer.
e) Turn off the monitor.

8.0 QC REQUIREMENTS

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements for method SW846 6010.

8.1 Method Detection Limits (MDLs). MDLs should be established for all analytes, using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level . MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

8.2 Linear Calibration ranges. The upper limit of the linear calibration ranges should be established for each analyte by determining the signal responses from three concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined whenever there is a significant change in

instrument response and every six months for those analytes that periodically approach their linear limit.

8.3 Initial Calibration Verification Standard (ICV). After each calibration, a standard from a different source than the calibration standard should be analyzed. For the ICV, all elements to be reported must be within 10 percent of the true value.

8.4 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain elements at less that the reporting limit for each element. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level . In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

8.5 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample with each set of samples. A minimum of one lab control sample is required for every 20 samples. Note: For soils, if a lab control is not available, a spike blank can be used. For a running batch, a new lab control sample is required for each different digestion day. Until sufficient lab control data become available (usually a minimum of 20 to 30 analyses) the laboratory should assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120 percent. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

8.6 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. The control limits for the matrix spike recovery are calculated on an annual basis and are used to assess whether a spike is in control. If a matrix spike is out of control, then the

results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the spike amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result)/Amount Spiked) x 100 = matrix spike recovery

8.7 Matrix Duplicate. The laboratory must digest a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. The duplicate rpd is calculated as shown below. The control limit for the duplicate recovery are calculated on an annual basis and are used to assess whether a duplicate is in control. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

8.8 Continuing Calibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 10 percent of the true value, the CCV should be reanalyzed to confirm the initial value. If the CCV is not within 10 percent of the true value after the reanalysis, no samples can be reported in the area bracketed by the failing CCV. The CCV must be made from an alternate source from the calibration curve.

8.9 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit for each element, then no samples can be reported in the area bracketed by the failing CCB.

8.10 Serial Dilution Analysis. For one sample per preparation batch, or whenever matrix interferences are

suspected for a batch of samples, a serial dilution should be prepared. For the serial dilution, a 1:5 dilution should be made on the sample. The results of the 1:5 dilution should agree within 10 percent of the true value as long as the sample and the dilution result are greater than 10 times the method detection limit and/or greater than 50 times the IDL. If the dilution does not agree, then the sample should be reported with a footnote indicating that there were possible matrix interferences. Alternatively, a serial dilution can be done with larger dilutions, and the sample can be reported from the dilutions. For example, a sample that failed the serial dilution criteria using the straight sample and a 1:5 dilution may pass the serial dilution criteria using a 1:2 dilution and a 1:10 dilution. In that case, the sample would be reported from the 1:2 dilution and the results would be footnoted that a dilution was required due to matrix interference. The calculation to be used for serial dilutions is shown below.

((Sample Result - Serial Dil. Result)/Sample Result) x 100 = Serial Dilution RPD

8.11 High Standard Check. After the instrument is properly calibrated, the high standard(s) should be reanalyzed for each element. (Note: The standards can be combined into one solution for this analysis). The analyzed value must be within 5 percent of the true value or that element should be recalibrated.

9.0 GLASSWARE CLEANING

All glassware must be washed with soap and tap water and then soaked in a 5% nitric acid bath for several hours. It must then be rinsed at least 3 times with distilled, deionized water.

10.0 DOCUMENTATION REQUIREMENTS

Refer to the Laboratory Quality Assurance Manual for documentation requirements.

11.0 SAFETY

The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with

plenty of water. If acids contact any part of the body, flush with water and contact the supervisor. Make sure to follow proper safety when working with gas cylinders.

12.0 CALCULATIONS

For water samples, the following calculations should be used. Refer to the QC section for the calculations to be used for the QC samples.

original sample concentration of metal (ug/l) =

$$\frac{\text{(conc. in the digestate (ug/l)) x (final digestate volume (ml))}}{\text{(initial sample volume (ml))}}$$

For soil samples, the following calculations should be used.

concentration of the metal in the dry sample (mg/kg) =

$$\frac{\text{(conc. in the digestate (mg/l) x final digestate volume(L))}}{\text{(sample wt. (kg)) x (\% solids/100)}}$$

13.0 INSTRUMENT MAINTENANCE

Recommended periodic maintenance includes the items outlined below. All maintenance must be recorded in the instrument maintenance log. In addition, the date of the maintenance should be filled in on the maintenance chart shown in Figure 1. The maintenance chart should be posted by each instrument so that instrument maintenance is kept up to date.

13.1 Change the pump tubing weekly or as needed.

13.2 Clean the filter on the recirculating pump approximately once a month and dust off the power supply vents every one to two weeks.

13.3 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

13.4 Change the sampler tip as needed (every one to two months).

13.5 Clean the recirculating pump lines every 3 months or more often if needed.

13.6 Clean the slides on the autosampler with methanol and wipe them with a KimWipe saturated with teflong spray a minimum of once per day.

13.7 For the TJA Trace, check and clean the following filters every one to two weeks:

- 2 filters on the back of the polychromator controller compartment
- one filter on the back of the power source
- one filter below the torch compartment

13.8 For the TJA Trace, check and change the oil on the vacuum pump at a minimum of once every 6 months or whenever the vacuum is greater than 25.

TABLE 1: REPORTING LIMIT BY ELEMENT

Analyte	Water Reporting Limit (ug/L)	Soil Reporting Limit (mg/kg)	TCLP Reporting Limit (mg/L)
Aluminum	200	20	
Antimony	5	6	
Arsenic	5	1	0.50
Barium	200	20	1.0
Beryllium	5	0.5	
Cadmium	4	0.5	0.005
Calcium	5000	500	
Chromium	10	1	0.010
Cobalt	50	5	
Copper	25	2.5	
Iron	100	10	
Lead	3	10	0.50
Magnesium	5000	500	
Manganese	15	1.5	
Nickel	40	4.0	
Potassium	5000	500	
Selenium	5	1	0.50
Silver	10	1	0.010
Sodium	5000	500	
Thallium	5	1	
Vanadium	50	5	
Zinc	20	2	

TABLE 2A: TJA 61E ANALYSIS LINES

Element	Wavelength
Al	308.215
As	193.696
Ca	317.933
Fe	259.940
Mg	279.078
Mn	257.610
Pb	220.353
Se	196.026
Tl	190.864
V	292.402
Ag	328.068
Ba	493.409
Be	313.042
Cd	226.502
Co	228.616
Cr	267.716
Cu	324.754
K	766.491
Na	588.995
Ni	231.604
Sb	206.838
Zn	213.856

TABLE 2B. TJA TRACE ANALYSIS LINES

Element	Wavelength	
Al	308.215	
As	189.042	
Ca	317.933	
Fe	271.441	
Mg	279.078	
Mn	257.610	
Pb	220.353	(a)
Se	196.026	(a)
Tl	190.864	
V	292.402	
Ag	328.068	
Ba	493.409	
Be	313.042	
Cd	226.502	
Co	228.616	
Cr	267.716	
Cu	324.753	
K	766.491	
Na	588.991	
Ni	231.604	
Sb	206.838	(a)
Zn	213.856	

(a) This element has two lines at this wavelength so that Crawford-Kunselman Noise Reduction techniques can be applied.

TABLE 3: SUGGESTED HIGH STANDARD LEVELS

Element	Suggested Level in ug/l
Ba	4000
Be	4000
Cd	4000
Cr	4000
As	4000
Se	4000
Pb	4000
Ql	4000
Mn	4000
Co	4000
Zn	4000
Cu	4000
Ni	4000
Na	4000
Sb	4000
Mo	4000
B	4000
Ag	500
Sb	4000
V	4000
Al	4000
Ca	4000
Fe	4000
Mg	4000
K	20000
Na	4000

TABLE 4: CONCENTRATIONS OF METALS IN THE MATRIX SPIKE

Element	Soils Final Concentration in mg/kg	TCLP Leachates Final Concentration in mg/l
Ag	10	0.050
Al	5000	
As	400	2.0
B	100	
Ba	400	10
Be	10	
Ca	1250	
Cd	10	0.050
Co	100	
Cr	40	0.20
Cu	50	
Fe	5000	
K	1250	
Mg	1250	
Mn	100	
Mo	100	
Na	1250	
Ni	100	
Pb	100	2.0
Sb	100	
Se	400	2.0
Tl	400	
V	100	
Zn	100	

FIGURE 1: INSTRUMENT MAINTENANCE LOG

Maintenance Needed	Required Frequency	Date Completed	Date Completed	Date Completed	Date Completed	Date Completed	Date Completed	Date Completed	Date Completed
Change pump tubing	weekly or as req.								
Clean recir. pump filter	monthly or as req.								
Dust power supply vents	weekly or as req.								
Clean or change nebulizer	biweekly or as req.								
Clean or change torch/injector tube	biweekly or as req.								
Change sampler tip	monthly or as req.								
Clean recir. pump lines	bimonthly or as req.								
Kimwipe slides on autosampler	daily								
Clean filters on instrument	weekly or as req.								
Change vacuum pump oil	twice/year or as req.								

Maintenance Needed	Required Frequency	Date Completed	Date Completed	Date Completed	Date Completed	Date Completed	Date Completed	Date Completed	Date Completed
Change pump tubing	weekly or as req.								
Clean recir. pump filter	monthly or as req.								
Dust power supply vents	weekly or as req.								
Clean or change nebulizer	biweekly or as req.								
Clean or change torch/injector tube	biweekly or as req.								
Change sampler tip	monthly or as req.								
Clean recir. pump lines	bimonthly or as req.								
Kimwipe slides on autosampler	daily								
Clean filters on instrument	weekly or as req.								
Change vacuum pump oil	twice/year or as req.								

Proposed Quantitation Limits for Final Effluent Analyses
Summit National Superfund Site
Deerfield Township of Portage County, Ohio

Element	Requested Quantitation Limit (ug/l)	OEPA Discharge Limits	Accutest Proposed Quantitation Limit	Accutest Current IDL Values (ug/l)
Antimony	7	5	5	1.7
Arsenic	3	7	5	2.5
Iron	20	300	100	24
Aluminum	50	536	200	37
Barium	5	219	5	0.4
Calcium	100	201785	1000	27
Chromium	10	5	5	0.6
Cobalt	10	14	10	0.5
Copper	1	2	2	1.1
Lead	1	1	1	1
Magnesium	50	72151	1000	16
Manganese	5	6818	5	0.6
Nickel	20	14	10	1.4
Potassium	200	6415	1000	16
Zinc	10	188	10	1.2

* Results can be reported to the IDL, but the values between the IDL and the proposed quantitation limits will be flagged with a B as estimated values. IDL values change on a quarterly basis.

Analyses done with SW846 methodologies.

Rev. Date: 10/07/96
F/N AAP055.SOP
Lab. Manager: JJ Cole
QA Manager: [signature]

TEST NAME: COLD VAPOR ANALYSIS OF MERCURY FOR WATER SAMPLES. (*CLP AND NON-CLP PROTOCOLS*)

LAB AREA: AA

TEST CODE: Hg

REPORTING LIMIT: 0.20 ug/l for waters.
0.001 mg/l for TCLP leachates.

1.0 SCOPE AND APPLICATION

This method can be applied to surface and saline waters and to domestic and industrial wastes. This SOP is based on the following methods: EPA 245.1 from "Methods for Chemical Analysis of Water and Wastes", March 1983, SW846 method 7470A, November 1992 revision, and EPA 245.1 CLP-M from ILMO2.0. Note: For drinking waters, refer to SOP AP055A.DOC which is based on the May 1994 revision of EPA method 245.1.

2.0 PRESERVATION

All liquid samples should be preserved by acidification with nitric acid to a pH of 2 or lower.

3.0 HOLDING TIME

All non-CLP samples should be analyzed within 28 days of the date of collection. All CLP samples should be analyzed within 26 days of the verified time of sample receipt.

4.0 INTERFERENCES

Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations of sulfide as sodium sulfide as high as 20 mg/l do not interfere with mercury recoveries when following this method. High copper concentrations (> 10 mg/l) may also interfere with mercury recoveries. Samples that are high in chloride such as seawater, brine, and industrial effluent may require as much as 25 ml of additional permanganate.

NOTE: When chloride concentrations are high, hydroxylamine sulfate and stannous sulfate should be used in place of the corresponding chlorides.

Finally, certain volatile organic materials will also absorb at this wavelength and can interfere. It can be determined if this type of interference is present by doing a preliminary run without reagents.

5.0 APPARATUS

5.1 A Fisher Mercury analyzer model HG-4 (a dual wavelength ratio spectrophotometer) is used for all analyses. Refer to the instrument manual for further details on this instrumentation.

5.2 Water bath, capable of maintaining a temperature of 95°C.

5.3 BOD Bottles, made of heat resistant glass.

6.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required.

6.1 Sulfuric acid, concentrated.

6.2 Sulfuric acid, 0.5 N. Add 14.0 ml of concentrated sulfuric acid to 0.5 liters of water. Dilute to 1 liter with water and mix well. **CAUTION**: always add acid to water.

6.3 Nitric acid, concentrated. This acid must have a low mercury content.

6.4 Stannous chloride. Add 50 g of stannous chloride to 500 ml of 0.5 N sulfuric acid and dissolve. This compound does not dissolve well and should be stirred continuously when in use. Stannous sulfate may be used in place of stannous chloride.

6.5 Sodium chloride-Hydroxylamine hydrochloride. Add 90 g of sodium chloride and 90 g of hydroxylamine hydrochloride to 750 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

6.6 Potassium Permanganate, 5 percent solution, w/v. Add 37.5 g of potassium permanganate to 750 ml of water and mix well. **CAUTION**: Potassium permanganate is a strong oxidizing agent. Handle with care.

6.7 Potassium persulfate, 5 percent solution, w/v. Add 37.5 g of potassium persulfate to 750 ml of water and mix well. **CAUTION**: Potassium persulfate is a strong oxidizing agent. Handle with care.

6.8 Mercury standard solutions.

6.8.1 10 ppm Hg solution. Using a 10 mL volumetric pipet, add 10 mL of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 1.00 L volumetric flask containing approximately 750 mL of water and 10 mL of concentrated nitric acid. Dilute to volume with water and mix well.

6.8.2 100 ppb Hg solution. Using a 10 mL volumetric pipet, add 10 mL of 10 ppm Hg solution to a 1.00 L volumetric flask containing approximately 750 mL of water and 10 mL of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard should be made fresh daily.

6.8.3 50 ppb Hg solution. Using a class A volumetric cylinder, add 50.0 ml of 100 ppb Hg solution to a 100 mL volumetric flask containing approximately 30 mL of DI water and 2 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard should be made fresh daily.

6.8.4 10 ppb Hg solution. Using a 20.0 mL volumetric pipet, add 20.0 ml of 100 ppb Hg solution to a 200 mL volumetric flask containing approximately 150 mL of DI water and 2 mL of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard should be made fresh daily.

6.9 Magnesium Perchlorate (drying agent). Remove spent magnesium perchlorate from the drying tube by gently tapping. The spent magnesium perchlorate should be dissolved in tap water and flushed down the drain. Recap the drying tube with fresh, anhydrous magnesium perchlorate. **Caution** Magnesium perchlorate is an oxidizer and an irritant. All handling of this chemical should be done in a hood.

7.0 WATER DIGESTION AND ANALYSIS PROCEDURE

Below is a step-by-step procedure for the digestion and analysis of water samples for mercury.

7.1 All BOD bottles should be soaked in 10% nitric acid overnight between uses. Each bottle should be triple rinsed with distilled, deionized water before use.

7.2 Make up the standard curve as shown below. Make sure to clearly label each bottle. Since the total amount of Hg in the bottle is what is measured, the amount of water added does not have to be exact. An easy way to do this is to put a 100 ml mark on the BOD bottles and always dilute to that mark.

mL of 10 ppb Hg solution	mL of 100 ppb Hg solution	mL of DI water	Total ug of Hg	ug/L of Hg
0.000	0.000	100	0.000	0.000
2.00	0.000	98	0.020	0.20
5.00	0.000	95	0.050	0.50
0.00	1.00	99	0.100	1.00
0.00	2.00	98	0.200	2.00
0.00	3.00	97	0.300	3.00
0.00	4.00	96	0.400	4.00
0.00	5.00	95	0.500	5.00

7.3 Make up the quality control samples as shown below. Make sure to clearly label each bottle. Note: multiple CCV checks are required for each run. Prepare a minimum of one CCV check for every 10 samples. For all analyses, the ICV must be from a separate source than the calibration curve. For CLP, both the CCV checks and the ICV check must be from a separate source than the calibration curve.

Sample ID	mL of 100 ppb Hg solution	mL of 50 ppb Hg solution	mL of DI water	Total ug of Hg	ug/L of Hg
Spike Blank	2.0	0.0	8.0	0.20	2.0
CCV Check	0.0	5.0	5.0	0.25	2.5
MB #1	0.0	0.0	10	0.0	0.0
MB #2	0	0.0	10	0.0	0.0
MS(non-CLP)	2.0	0.0	8.0	.20*	2.0*
MS (CLP)	1.0	0.0	9.0	.10*	1.0*
Duplicate	0.0	0.0	10	0.0	0.0
ICV	0.0	5.0	5.0	.25	2.5

* plus the level of Hg in the sample.

7.4 Samples. If no information is available about the level of mercury in the samples to be analyzed, set up a 100 ml sample size. If information is available, select a sample size that will result in an analysis value near the mid-range of the curve. Record the volume used on the sample analysis data sheet.

7.5 To all samples, QC and standards add the reagents listed below, swirling the samples well after each addition of reagent. More potassium permanganate solution may be required for some samples. Enough potassium permanganate should be added so that the purple color persists for at least 15 minutes.

2.5 ml of conc. nitric acid.
5 ml of conc. sulfuric acid.
15 ml of permanganate solution.

7.6 After the purple color is stabilized (at least 15 minutes after the addition of the potassium permanganate), then add 8 ml of persulfate solution.

7.7 Cover the samples, standards, and QC and place them in a room temperature water bath. Increase the temperature to 95^0 C. After the bath has reached 95^0 C, heat the samples for 2 hours. Then remove and cool.

7.8 While the samples are digesting, begin setting up the Fisher Mercury analyzer following the steps outlined below. Additional instructions are available in the instrument operators manual.

7.8.1 Turn on the nitrogen and adjust to 2 L/minute. Turn on the instrument power.

7.8.2 Change magnesium perchlorate dessicant. Do not connect the drying tube to the instrument until after the gas is turned on to make sure that no dust gets into the instrument.

7.8.3 Set the controls on the instrument as follows:
ZERO SET control to mid-position.
MANUAL/AUTO switch to manual.
10X/50X switch to center position (1X).
Damping control to mid-position.
AGC button to off position (out).
LAMP A to full counterclockwise position.

LAMP B to full counterclockwise position.
AGC adjustment to mid-position.

7.8.4 Turn LAMP B control clockwise until the percent absorption meter reads 100.

7.8.5 After 10 minutes, press AGC switch on (in).

7.8.6 Turn AGC adjustment until the percent absorption meter reads 100.

7.8.7 Turn LAMP A clockwise until the percent absorption meter reads zero.

7.8.8 Allow 15 minutes for warm-up and then readjust LAMP A as necessary to keep it at zero. (Fine adjustment can be made on the front of the instrument.)

7.8.9 Set 10X/50X switch to 10X for initial analysis. The needle should drop to just below zero.

7.9 Add 6 mL of hydroxylamine hydrochloride solution to each standard and sample to reduce the excess permanganate. Swirl the samples until the solution has been completely decolorized. Then purge the air space in the top of each BOD bottle with nitrogen to remove any volatile organics.

7.10 Add 5 ml of stannous chloride solution to each sample immediately before analysis. Quickly place the bubbler tube in the BOD bottle and watch the absorbance meter. Record the maximum absorbance reading obtained on the analysis data sheet by the proper sample or standard ID.

7.10.1 Do not remove the bubbler tube from the BOD bottle until the absorbance has returned to its minimum value unless the bottle under the hood.

7.11 Calculate the standard curve by linear regression. Verify that the correlation coefficient of the curve is $\geq$ 0.995 and that the intercept of the curve is less than the reporting limit. If the curve is not within acceptable limits, then the curve should be redigested and reanalyzed before any samples are analyzed.

7.12 Repeat steps 8 and 9 for the samples. The results should be calculated using the linear curve generated above. Make sure to bracket every 10 samples with CCV and CCB checks.

8.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

8.1 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses

LAMP B to full counterclockwise position.
AGC adjustment to mid-position.

7.8.4 Turn LAMP B control clockwise until the percent absorption meter reads 100.

7.8.5 After 10 minutes, press AGC switch on (in).

7.8.6 Turn AGC adjustment until the percent absorption meter reads 100.

7.8.7 Turn LAMP A clockwise until the percent absorption meter reads zero.

7.8.8 Allow 15 minutes for warm-up and then readjust LAMP A as necessary to keep it at zero. (Fine adjustment can be made on the front of the instrument.)

7.8.9 Set 10X/50X switch to 10X for initial analysis. The needle should drop to just below zero.

7.9 Add 6 mL of hydroxylamine hydrochloride solution to each standard and sample to reduce the excess permanganate. Swirl the samples until the solution has been completely decolorized. Then purge the air space in the top of each BOD bottle with nitrogen to remove any volatile organics.

7.10 Add 5 ml of stannous chloride solution to each sample immediately before analysis. Quickly place the bubbler tube in the BOD bottle and watch the absorbance meter. Record the maximum absorbance reading obtained on the analysis data sheet by the proper sample or standard ID.

7.10.1 Do not remove the bubbler tube from the BOD bottle until the absorbance has returned to its minimum value unless the bottle under the hood.

7.11 Calculate the standard curve by linear regression. Verify that the correlation coefficient of the curve is $\geq$ 0.995 and that the intercept of the curve is less than the reporting limit. If the curve is not within acceptable limits, then the curve should be redigested and reanalyzed before any samples are analyzed.

7.12 Repeat steps 8 and 9 for the samples. The results should be calculated using the linear curve generated above. Make sure to bracket every 10 samples with CCV and CCB checks.

8.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

8.1 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses

by 3.14, which is the student's t value for a 99% confidence level . MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response. Note: For CLP protocols, MDL studies are not required. However, see IDL requirements below.

8.2 Instrument Detection Limits (IDLs). The instrument detection limits are determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of 7 consecutive replicates of a standard solution at a concentration from 3 to 5 times the estimated detection limit. IDLs must be done quarterly for each instrument.

8.3 Quality Control Sample (also referred to as Initial Calibration Verification Standard (ICV)). During each analysis, a standard from a different source than the calibration standard should be analyzed. Normally this is analyzed at the beginning of the run. For this method, the ICV should be within 20 percent of the true value. For CLP, the ICV must be at a concentration other than that used for instrument calibration, but within the calibration range.

8.4 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain mercury at less that the reporting limit or less than the CRDL. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level . In addition, for non-CLP work, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

8.5 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample with each set of samples. A minimum of one lab control sample is required for every 20 samples. For a running batch, a new lab control sample is required for each different digestion day. Until sufficient lab control data become available (usually a minimum of 20 to 30 analyses) the laboratory should assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120 percent. (Note: for CLP, limits of 80 to 120 percent are always applied.) For non-CLP work, if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag.

8.6 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples.

8.6.1 For non-CLP samples, the control limits for the matrix spike recovery are calculated on an annual basis and are used to assess whether a spike is in control. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

8.6.2 For CLP samples, the spike recovery should be within the limits of 75 to 125. An exception to this rule occurs where the sample concentration exceeds the spike concentration by a factor of 4 or more.

8.6.3 Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculation shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

8.7 Matrix Duplicate. The laboratory must digest a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. The duplicate rpd is calculated as shown below.

8.7.1 For non-CLP samples, the control limits for the duplicates are calculated on an annual basis and are used to assess whether a duplicate is in control. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

8.7.2 For CLP samples, the duplicate rpd should be within the limits of $\pm$ 20 percent. An exception to this rule occurs where the sample and the duplicate are less than 5 times the CRDL and are within a range of $\pm$ the CRDL, then the duplicate is considered to be in control.

8.7.3 Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculation shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \text{\% RPD}$$

8.8 Continuing Calibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 20 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: for non-CLP samples, the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

8.9 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit or the CRDL, then no samples can be reported in the area bracketed by the failing CCB.

9.0 DOCUMENTATION REQUIREMENTS:

Refer to the laboratory Quality Assurance Manual for all documentation requirements.

9.1 Sample Worksheets. Attached are the analysis data sheets for the Hg water samples. Make sure to record the start time, end time and temperature for all digestions. All sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure should be noted in the comments sections. Make sure that all dilutions are clearly documented.

9.2 Standards and Reagents. All standards and reagents must be recorded in the reagent log book.

10.0 SAFETY:

The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual. Particular care should be observed in handling the strong acids and oxidizing agents.

11.0 CALCULATIONS:

The calculations which should be used for water samples are shown below.

$$\text{Soil conc. in ug/L} = \frac{\text{sample conc. in ug/l x final volume in ml}}{\text{initial volume in mL.}}$$

Example: An absorbance of 5.6 was obtained after analyzing a sample. This corresponded to a value of 1.08 ug/L. The volume of the sample analyzed was 100 ml and the final volume was 100 ml.

$$(1.08 \text{ ug/L} \times 100 \text{ ml})/(100 \text{ ml}) = 1.08 \text{ ug/L}$$

12.0 INSTRUMENT MAINTENANCE:

12.1 Clean the cell as required to make sure that a clear optical path is maintained.

12.2 Change the lamps as needed.

12.3 Clean the exterior of the instrument as needed.

12.4 Complete any other maintenance required to keep the instrument if good running order.

TEST NAME: **Cyanide (Lachat Autoanalyzer).**

LAB AREA: GN

TEST CODE: CN

METHOD REFERENCE: EPA 335.2 for wastewaters
EPA 335.4 for drinking waters
SW846 9010 for soils

REPORTING LIMIT: 0.010 mg/l for waters, 1.0 mg/kg for soils

1.0 SCOPE AND APPLICATION

The purpose of this method is to determine the amount of total cyanide in any given sample. The sample is distilled prior to analysis to remove interferences. The distilled cyanide is reacted with chloramine-T at a pH of less than 8 to form cyanogen chloride. The cyanogen chloride is then reacted with pyridine-barbituric acid reagent to form a red-blue dye. The intensity of the dye is measured by recording the absorbance at 570 nm.

2.0 HOLDING TIME

All cyanides should be analyzed within 14 days of the date of collection. (Note: CLP cyanides should be analyzed within 12 days from the verified time of sample receipt. Refer to the CLP cyanide SOP and the CLP SOW for further details on the analysis of samples for CN following CLP protocols.)

3.0 PRESERVATION

Water samples should be preserved with sodium hydroxide to a pH of $\geq$ 12 and cooled to 4 °C at the time of collection. Ascorbic acid should also be added to samples that are suspected to contain oxidizing agents such as chlorine. Soil samples should be cooled to 4°C at the time of collection.

4.0 INTERFERENCES

Many of the interferences in this method can be reduced or eliminated by the distillation step. All samples should be distilled before analysis. Sulfides can cause interferences but these can be removed by treatment of the distillate with cadmium or lead carbonate solution. High results may also be obtained due to interferences from nitrate or nitrite. These interferences can be eliminated by pretreatment of the sample with sulfamic acid during the distillation step. Oxidizing agents interfere by decomposing most of the cyanide. Ascorbic acid, added to the sample at the time of collection, will minimize the effect of these oxidizing agents.

5.0 APPARATUS

5.1 Automated continuous flow analyzer designed to deliver and react sample and reagents in the required order and ratios. Currently, the Lachat QuikChem AE Automated Ion Analyzer is being used.

5.1.1 Autosampler

5.1.2 Multichannel pump

5.1.3 Reaction manifold.

5.1.4 Colorimetric detector

5.1.5 Real time data acquisition device (either electronic or hard copies.)

5.2 Balance. Analytical balance capable of accurately weighing to the nearest 0.0001 g.

5.3 Volumetric glassware. Class A volumetric pipets and flasks as required.

6.0 REAGENTS

All reagents should be made from ACS grade reagents unless otherwise noted. Distilled deionized water should be used whenever water is needed.

6.1 Carrier solution, 0.25 M Sodium Hydroxide. Dissolve 10.0g of sodium hydroxide in a 1 liter volumetric flask containing approximately 800 ml of DI water. Dilute to a final volume of 1 liter and mix well.

6.2 1.25 N Sodium Hydroxide Solution (for preparation of standards). Dissolve 10.0 g of sodium hydroxide in a 200 ml volumetric flask containing approximately 160 ml of DI water. Dilute to a final volume of 200 ml and mix well.

6.3 Phosphate Buffer Solution, 0.71M. Dissolve 97 g of anhydrous potassium dihydrogen phosphate (potassium phosphate, monobasic, anhydrous, KH2PO4) in approximately 800 ml of DI water. Dilute to a final volume of 1 liter and mix well.

6.4 Chloramine-T Soution. Add 2.0 g of chloramine-T to a 500 ml volumetric flask containing approximately 250 ml of DI water. Dilute to a final volume of 500 ml with DI water and mix well. Note: This reagent should be prepared fresh weekly.

6.5 Pyridine-Barbituric Acid Reagent. Note: Prepare this reagent in a hood. Weigh 15.0 g of barbituric acid in 1 liter volumetric flask. Add 100.0 ml of water, rinsing down the sides of the flask to wet the barbituric acid. Add 75 ml of pyridine with stirring and mix until the barbituric acid dissolves. Then add 15 ml of concentrated hydrochloric acid and mix. Dilute to a final volume of 1 liter with DI water and mix well.

6.6 Cyanide Stock Solution, 1000 mg/l. Dissolve 2.51 g of KCN and 2.0 g of KOH in approximately 900 ml of DI water in a 1 liter volumetric flask. Dilute to a final volume of 1 liter. Standardize weekly with silver nitrate solution.

6.7 Standard Silver Nitrate Solution, 0.0192 N: Crush approximately 5 g of silver nitrate crystals and dry to constant weight at 40 C. Weigh out 3.2647 g of dried silver nitrate into a 1 liter flask containing approximately 800 ml of DI water. Dilute to a final volume of 1 liter with DI water and mix well.

6.8 Intermediate Cyanide Solution, 20.0 mg/l.. Pipet 10.0 mL of 1000 mg/l stock solution of CN into a 500 ml volumetric flask containing approximately 400 ml of DI water. Dilute to a final volume of 500 ml and mix well.

6.9 Intermediate Cyanide Solution, 2.0 mg/l. Pipet 10.0 mL of 20.0 mg/l cyanide solution into a 100 ml volumetric flask containing approximately 80 ml of DI water. Dilute to a final volume of 100 ml and mix well.

6.10 Cyanide Standard Solutions. All standards are made up using the above intermediate solutions as outlined in the table below. All standards should have a final concentration of 0.25 N NaOH. This NaOH concentration can be obtained by adding 20 ml of 1.25 N NaOH to each of the standards.

ml of 20.0 mg/l CN	ml of 2.0 mg/l CN	Final Volume	Concentration (mg/l)
4.0 ml	0.0 ml	100 ml	0.80 mg/l
3.0 ml	0.0 ml	100 ml	0.60 mg/l
2.0 ml	0.0 ml	100 ml	0.40 mg/l
0.0 ml	10.0 ml	100 ml	0.20 mg/l
0.0 ml	5.0 ml	100 ml	0.10 mg/l
0.0 ml	1.0 ml	100 ml	0.020 mg/l

7.0 PROCEDURE

Below is a step-by-step procedure for the analysis of samples for the determination of cyanide. At the end of this SOP is a short summary outlining the overall procedure.

7.1 If the cyanide stock solution has not been standardized within a week, then the stock must be standardized before proceeding further with the analysis. The standardization can be done following the procedure outlined below.

7.1.1 Volumetrically measure out 25.0 ml of the 1000 mg/l cyanide stock solution into a graduated plastic beaker. Add 10 to 12 drops of benzalrhodanine indicator to the solution. Place a stir bar in the beaker.

7.1.2 Fill a buret with 0.0192 N silver nitrate solution. Titrate the sample with continuous stirring until the color changes from yellow to a brownish-pink. Approximately 25 ml of silver nitrate solution should be needed to reach this endpoint. Also analyze a method blank that has been brought to pH > 12 with KOH following this procedure.

7.1.3 Calculate the concentration of the stock cyanide solution using the equation shown below.

$$CN, mg/l = \frac{(A - B) \times 1000}{25 ml}$$

Where A = the volume of $AgNO_3$ used to titrate the sample.
B = the volume of $AgNO_3$ used to titrate the blank.

Make sure to correct the concentrations of the standard solutions based on the true concentration of the stock solution.

7.2 Install the cyanide reaction manifold. Check all tubing and change any tubing that is flat, dirty, etc. Install the appropriate sample loop and the appropriate filter. Place the tubing in the bottles for the pyridine/barbituric acid, the chloramine-T, the phosphate buffer, and the 0.25 M NaOH carrier. Also make sure that the waste container is in place. Refer to the attached diagram for additional information.

7.3 Start pumping reagents through the system.

7.4 Select the "Methods" option in the QuikChem AE Main Menu and go to "Analysis Select and Download". Select the appropriate method. Note: If an appropriate method is not available, then contact the lab supervisor or manager and refer to the Lachat manuals for help in creating a new method.

7.5 Select the "Samples" option in the QuickChem AE Main Menu and go to "Tray Definition and Submit". The system will now be in the default template. If you are going to use a different template, then go to the "File" option and pick the option "Read Template (Method)".

7.6 Load your standards in the autosampler. In the software, go to the "Submit" option and pick the option "Calibrate Now". The instrument will now start calibrating. Note: The calibration may also be combined with running the samples by using the "Submit Current Tray" option and answering Y to the option to calibrate before running the samples.

7.7 Move to the "Identification" option of the software. This can be done while the instrument is calibrating. Enter in the samples and QC (Method blanks, spike blanks, duplicates, and matrix spikes). Also enter the initial weights and/or volumes and final volumes and dilution factors at this point. Other QC samples (CCV's, CCB's, and ICV's) are automatically defined and do not need to be included as separate samples in the tray. Pour the distilled samples into the autosampler cups and put them in the tray as you are defining the tray. Refer to Section 8 for further information on QC requirements. Note: samples must always be distilled before analysis.

7.8 After you have finished defining the tray, go to "File" and "Write Template (Method)" to save this information. Enter "savetray" as the template name and overwrite the previous savetray file.

Note: If you are calibrating and running the samples at the same time, you will not have to save the file as described above. It will automatically saved when the tray is submitted.

7.9 If the calibration meets the method criteria, it will be automatrically approved by the software. (Alternatively, this can be done manually in the "Results/Approval" option.) If the calibration did not meet the method criteria, then the instrument should be recalibrated at this point. Then go to the

"Samples", "Tray Definition and Submit" menu and choose the "Submit" option. Go to "Submit Current Tray" and answer N to the option to calibrate before running the samples.

7.10 If there are problems during the analysis, the run can be aborted using the "Kill Tray" command, located in the "Submit" option.

7.11 When the run is complete print out the report using the "Reports" option under the "Results/Approval" menu. An export file may also need to be generated. Check with the supervisor or manager for more information on this area.

7.13 At the end of the run, rinse out the remainder of the system with DI water.

7.14 Review data and assemble a data package including the following items:

- Results report, showing dilution and weight correction factors.
- Quality control sheets.
- Control chart for external.
- Printout of peaks.
- Distillation or digestion log.
- Computer workgroup sheets.

8.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

8.1 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level . MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

8.2 Linear Dynamic Range (LDR). For each instrument, the upper limit of the linear dynamic range must be established. A linear calibration should be prepared from 3 standards, one of which is close to the upper limit of the linear range. The LDR is determined by analyzing succeedingly higher standard concentrations of an analyte until the observed analyte concentration is no more than 10 percent below the true value of the standard.

8.3 Quality Control Sample (also referred to as Initial Calibration Verification Standard, (ICV)). At a minimum of once per quarter, a standard from a different source than the calibration standard must be analyzed. Normally this is analyzed at the beginning of the run after the CCV and CCB checks. For this method, the ICV should be within 10 percent of the true value. Note: It is recommended that this standard be analyzed with each run.

8.4 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain the analyte at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level . In addition, if all the samples

are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

8.5 Spike Blank. The laboratory must digest and analyze a spike blank with each set of samples. A minimum of one spike blank is required for every 20 samples. Until sufficient lab control data become available (usually a minimum of 20 to 30 analyses) the laboratory should assess laboratory performance of the spike blank for non-potable samples against recovery limits of 80 to 120 percent. For drinking water samples, the lab control should be in the limits of 90 to 110 percent. If the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag.

8.6 Calibration Curve. Each day a calibration curve consisting of 5 points and a blank must be run. The calibration curve should have a correlation coefficient of at least 0.995 and the concentration intercept must be less than the reporting limit for the method. Note: For cyanides, it is recommended that at least 2 standards (a high and a low) be distilled and compared to similar values on the standard curve. The distilled standards should be within 10 percent of the true values.

8.7 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples.

8.7.1 For non-potable samples, the spike recovery should be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery should be applied. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

8.7.2 For drinking water samples, the spike recovery should be assessed against limits of 90 to 110 percent. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

8.7.3 Both the matrix spike recovery should be calculated as shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

8.8 Matrix Duplicate. The laboratory must digest a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. The duplicate rpd is calculated as shown below.

8.8.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD should be applied If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

8.8.2 The duplicate RPD should be calculated as shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \%\,\text{RPD}$$

8.9 Continuing Calibration Verification. (Also known as the instrument performance check solution.) Analyze the continuing calibration verification solution and the continuing calibration blank after the initial calibration, after every tenth sample, and at the end of the sample run. If the CCV solution is not within 10 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

8.10 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after the initial calibration, after every tenth sample, and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

9.0 CALCULATIONS

Calculations may be either done manually, using the Lachat software, or using the Accutest LIMS system. Check with the lab supervisor or manager for more instructions.

For water samples, the following calculations should be used.

original sample conc. of cyanide in mg/l =

$$\frac{\text{Calculated value in mg/l x final distillate volume (ml) x dilution factor}}{\text{initial sample volume (ml)}}$$

For soil samples, the following calculations should be used.

original sample conc. of cyanide in mg/kg =

$$\frac{\text{Calculated value in mg/l x final distillate volume (ml) x dilution factor}}{\text{initial sample volume (g) x (\%solids/100)}}$$

10.0 GLASSWARE CLEANING

All glassware should be washed with soap and tap water and then well rinsed with distilled, deionized water. It should then be baked in a 105^{0} C oven.

11.0 DOCUMENTATION REQUIREMENTS

Attached are the QC summary sheets run log sheets should be available for each run. Each analyst should review all data and assemble a data package consisting of the following information.

- Results report, showing dilution and weight correction factors.
- Quality control sheets.
- Control chart for external.
- Printout of peaks.
- Distillation or digestion log.
- Computer workgroup sheets.

In addition, all reagent information such as lot numbers should also be recorded in the reagent log book. Any unusual characteristics of the samples should be noted in the final results section of the final data report. Make sure that all sample ID's and dilutions are labeled on the data.

12.0 SAFETY

The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual. A lab coat and safety glasses should be used throughout the analysis. The appropriate gloves should be worn as needed.

13.0 PROCEDURE SUMMARY

The procedure outlined below is a summary for quick reference purposes only. Make sure to read and understand the entire SOP before starting an analysis.

a. Prepare reagents, standardize CN stock.
b. Insert the reaction module, connect all reagents, and start the instrument.
c. Pour the calibration standards and start calibrating.
d. Enter sample information into autosampler table. (Make sure to save this.)
e. Approve calibration.
f. Submit autosampler tray for analysis.
g. Print out peaks and results.
h. Review results and turn in to general chemistry supervisor.

Rev. Date: 05/14/93
F/N GNP101.SOP

Lab Mgr. TZ Cole
QA Mgr. _____

TEST NAME: HARDNESS AS $CaCO_3$.

LAB AREA: GN.

TEST CODE: HRD.

METHOD REFERENCE: EPA 130.2.

DETECTION LIMIT: 4.0 mg/l.

1.0 SCOPE AND APPLICATION

This method is used as a measure of the hardness in a samples and is applicable to all waters and waste waters. The method is based on EPA Method 130.2.

2.0 PRESERVATION

Water samples should be acidified to a pH of less than 2 by the addition of concentrated nitric acid and kept under refrigeration at 4^0 C until they are analyzed.

3.0 HOLDING TIME

All samples should be analyzed within 6 months of the date of collection.

4.0 INTERFERENCES

Some metal ions interfere by causing fading or indistinct endpoints or by stoichiometric consumption of EDTA. These interferences can be reduced by adding certain inhibitors before titration.

5.0 APPARATUS

The following items are needed for the analysis of samples following the method outlined below:

5.1 25 ml microburet.

5.2 Erlenmeyer flasks.

5.3 Stir bars.

5.4 Stir plates.

6.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required.

6.1 Buffer solution. Dissolve 1.179 g of disodium EDTA (analytical grade) and 780 mg of $MgSO4 \cdot 7H_2O$ (or 644 mg $MgCl_2 \cdot 6H_2O$) in 50 ml of DI water. Add this solution to a 250 ml volumetric flask containing 16.9 g of ammonium chloride (NH_4Cl) and 143 ml concentrated ammonium hydroxide (NH_4OH) with mixing and dilute to the mark with DI water. Store in a plastic bottle for no longer than 1 month.

6.2 Inhibitor solutions. These are to be used only if interferences are evident during the titration. Please check with lab supervisor or lab manager first.

6.2.1 Inhibitor I: NaCN powder. (**Caution** - extremely poisonous). Flush solutions or sample containing this down the drain using large quantities of water.
Make sure that there are no acids present that might liberate HCN.

6.2.2 Inhibitor II: Dissolve 5.0 g of $Na_2S\ 9H_2O$ in 100 ml of DI water. Cover with tightly fitted rubber stopper.

6.2.3 Inhibitor III: Dissolve 4.5 of hydroxylamine hydrochloride in 100 ml of 95 % ethanol or isopropanol.

6.3 Indicator. Solid calmagite or a calmagite indicator solution can be purchased commercially.

6.4 Standard EDTA titrant, 0.02 N. Place 3.723 g of analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, $Na_2H_2C_{10}H_{12}O_8N2{\cdot}2H_2O$ in a 1 liter volumetric flask and dilute to the mark with DI water. Check with standard calcium solution by titration. (See section 1 under procedure.) Store in polyethylene.

6.5 Standard calcium solution (1000 mg/L). Place 1.000 g of anhydrous calcium carbonate in a 500 ml flask. Slowly add 1:1 HCl until all of the $CaCO_3$ has dissolved. Cool. Add a few drops of methyl red indicator and adjust to intermediate orange color by adding 3N ammonium hydroxide (NH_4OH) or 1:1 HCl as required. Quantitatively transfer to a 1 l volumetric flask and dilute to the mark with distilled water.

6.6 Hydrochloric acid solution, 1:1.

6.7 Methyl red indicator. Dissolve 0.10 g methyl red in DI water in a 100 ml volumetric flask and dilute to the mark.

6.8 Ammonium hydroxide solution, 3 N. Dilute 210 ml of concentrated ammonium hydroxide (NH_4OH) to 1 liter with DI water.

6.9 Ammonium hydroxide solution, 1 N. Dilute 70 ml of concentrated ammonium hydroxide to 1 liter with DI water.

7.0 TITRATION PROCEDURE

Before starting on the samples, make sure that the EDTA solution has been standardized within the past month. To standardize the EDTA solution, follow the procedure outlined below.

7.1 Place 10.0 ml of standard calcium solution in a vessel containing about 50 ml of DI water. Add 1 ml of buffer solution and a few crystals of calgamite. Titrate slowly with continuous stirring with the EDTA until the last reddish tinge disappears. Add the last few drops at 3 to 5 second intervals. At the end point the color is blue. Total titration duration should be no more than 5 minutes from the time of the buffer addition. Perform this titration in duplicate. Calculate the normality of the EDTA as shown below.

N of EDTA = (0.20)/(ml of EDTA added)

7.2 Start the titration of the samples by measuring 25 ml of sample into the titration vessels. Set up a blank spike by adding 4.0 ml of standard calcium carbonate solution to a titration vessel containing approximately 25 mL of DI water and dilute to approximately 50 ml with DI water. Set up a matrix spike by adding 4.0 ml of standard calcium carbonate solution to the sample that is to be spiked. Neutralize the samples with 1 N ammonium hydroxide, and dilute to a final volume of approximately 50 ml. (Note: highly polluted samples should first go through a metals digestion step before analysis. Please check with lab supervisor or manager.)

7.3 Add 1 to 2 ml of buffer solution to each sample. Note: the pH of the samples at this point should be 10.0 to 10.1.

7.4 Add a few grains of the Calgamite to each sample.

7.5 Titrate the sample slowly with continuous stirring with the standard EDTA titrant until the last reddish tint disappears. The solution is normally blue at the end point. Note: Make sure that the titration is complete within 5 minutes of the time that the buffer solution is added in order to minimize calcium carbonate precipitation.

Note: If appears that interferences are present, repeat the titration as above, but add inhibitor immediately after step 3.

8.0 CALCULATIONS

For water samples, the following calculations should be used:

Hardness as mg $CaCO_3$/l = (A x N x 50000)/(ml sample).

whereA = ml of EDTA titrant.
N = normality of EDTA titrant.

NOTE 1: For all of the samples and quality control, a final volume of 25 mL should be used if following the procedure as outlined in this SOP.

NOTE 2: Make sure to use the normality and not the molarity of the EDTA titrant in this calculation.

9.0 QC REQUIREMENTS

An external and a method blank should be prepared with each batch of 20 samples or daily, whichever is more frequent. If an external quality control sample is not available, a spike blank may be substituted. The external should be within the range specified by the manufacturer and the spike blank should be within 80 to 120 percent of the true value. A duplicate sample and a matrix spike should be prepared for every 20 samples. All QC calculations should be done as outlined in the Accutest QC manual. QC limits are complied by Accutest quarterly and should be used to determine if a given analysis is valid.

10.0 GLASSWARE CLEANING

All glassware should be washed with soap and tap water and then well rinsed with distilled, deionized water.

11.0 DOCUMENTATION REQUIREMENTS

Attached is the data sheet to be used for the hardness analysis. Any unusual characteristics of the samples should be noted in the comments section. The EDTA standardization should be recorded in the standardization notebook. Make sure that all sample information is included on these sheets. In addition, all reagent information such as lot numbers, vendors, date made, etc. should be recorded in the reagent log book. Make sure that all samples ID's and dilutions are clearly labeled on the data. Place a copy of the completed analysis form in the hardness book. Fill in the control chart for the external quality control sample and attach a copy of the control chart to the analysis sheet and digestion log.

12.0 SAFETY

The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual. Note the special precautions under the inhibitor section for NaCN.

Rev. Date: 7/21/92
F/N GNP020.SOP
Lab Mgr. TT Cole
QA Mgr. [signature]

TEST NAME: TOTAL DISSOLVED SOLIDS (TOTAL FILTERABLE RESIDUE).

LAB AREA: GN

TEST CODE: TDS

METHOD REFERENCE: EPA 160.1

DETECTION LIMIT: 10 mg/l

1.0 SCOPE AND APPLICATION

This method is used to determine the amount of solids in a sample which are capable of passing through a glass fiber filter. The method is based on EPA Method 160.1 and is applicable to all waters and wastewaters.

2.0 PRESERVATION

Water samples should be refrigerated at 4^0 C until analysis.

3.0 HOLDING TIME

All samples should be analyzed within 7 days of the date of collection.

4.0 INTERFERENCES

4.1 Waters containing significant amounts of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

4.2 Samples containing high concentrations of bicarbonate will require prolonged drying at 180^0 C to ensure that all of the bicarbonate is converted to carbonate.

4.3 Total residue in a drying dish should be limited to approximately 200 mg. If there is too much residue in a dish, water may become trapped below the residue and give an artificially high TDS number.

5.0 APPARATUS

The following items are needed for the analysis of samples following the method outlined below:

Whatman 924-AH glass fiber filters.
Filter holder with filtering flask.
100 ml evaporating dishes.
Steam baths or hot plates.
Drying oven to be set at 180° C.
Desiccator.
4-place analytical balance.

6.0 REAGENTS

Distilled water should be used for all rinsing in this method.

7.0 PROCEDURE

Below is a step-by-step procedure for the analysis of samples for TDS.

7.1 Prepare evaporating dishes by heating the clean dish to 180° C for 1 hour. Cool in desiccator and store until needed. Weigh immediately before use.

7.2 Place a clean filter in the filter holder and place the filter holder on the filtering flask. Pour three 20 ml portions of DI water through the filter. Continue to apply a vacuum to the filter until no traces of water remain. Discard the rinsing water.

7.3 Shake the sample well and measure out 100 ml in a 100 ml graduated cylinder. Turn on the vacuum.

NOTE: A smaller sample size may be used if a very high TDS value is expected. For Method Blanks, use a 100 ml portion of DI water.

7.4 Filter the sample through the glass fiber filter. Rinse with three 10 ml portions of DI water. Continue to apply a vacuum to the filter until no traces of water remain.

7.5 Transfer the filtrate into the 100 ml evaporating dish and lightly cover the dish with foil.

NOTE: If the sample cannot be evaporated at once or if all of the sample will not fit into the evaporating dish put the extra sample into a labeled plastic beaker and cover with a lid.

7.6 Evaporate the sample to dryness in an oven at 105° C or on a steam bath.

7.7 Dry the evaporated sample for at least one hour at 180° C. Cool in a desiccator and weigh.

7.8 For samples with results greater than 2000 mg/l, repeat steps 7.1 to 7.7 using a smaller sample size.

NOTE: 10% of the samples should be redried and reweighed to ensure that the batch was properly processed.

8.0 CALCULATIONS

The following calculations should be used.

$$\frac{(A-B) * 1000 \text{ ml/l}}{(\text{sample volume in ml})}$$

where A = Weight of evaporating dish + dried sample in mg
B = Tare weigh of evaporating dish in mg

9.0 QC REQUIREMENTS

A duplicate sample and a method blank should be prepared with each set of 20 samples. 10% of the samples should be redried to confirm that the samples were dried properly. All QC calculations should be done as outlined in the Accutest QC manual. QC limits are compiled by Accutest and should be used to determine if a given analysis is valid.

10.0 GLASSWARE CLEANING

All glassware should be washed with soap and tap water and then well rinsed with distilled, deionized water. It should then be baked in a 180° C oven.

11.0 DOCUMENTATION REQUIREMENTS

Attached is the data sheet to be used for the TDS samples. Make sure that all sample information is included on these sheets. Any unusual characteristics of the samples should be noted in the comments section.

12.0 SAFETY

The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual.

Rev. Date: 12/03/93
F/N GNP087.SOP

Lab Manager: _____
QA Manager: _____

TEST NAME: TOTAL SUSPENDED SOLIDS (NON FILTERABLE RESIDUE)

LAB AREA: General chem.

TEST CODE: TSS

REFERENCE: EPA METHOD 160.2

DETECTION LIMIT: 4.0 mg/l.

1.0 SCOPE AND APPLICATION

This method is used to analyze the amount of residue in a liquid sample which cannot pass through a Whatman 934-AH filter.

2.0 PRESERVATION: Cool, 4^0 C.

3.0 HOLDING TIME: 7 Days from time of sampling.

4.0 APPARATUS

4.1 Glass micro fiber filters Whatman 934-AH (prepared as described below).

4.2 100 ml graduated cylinder.

4.3 Analytical balance (4 place).

4.4 Vacuum pump apparatus, with filter support.

4.5 1000 ml flask attached to vacuum.

4.6 Desiccator.

4.7 Tweezers.

4.8 Trays with grates for drying.

4.9 Oven at 103-105^0 C.

5.0 PROCEDURE

5.1 Place filter on filter support and rinse with three 20 ml portions of DI Water. Dry in a 103 - 105 °C oven for at least one hour, or until a constant weight can be obtained. Cool and store in a desiccator.

5.2 Immediately before the analysis, obtain the weight of the dried glass fileter (A) using a 4 place analytical balance.

5.3 Put prepped filter in Buchner funnel which is attached to a 250 ml or larger filtering flask.

5.4 Pour 100 ml of sample into funnel.

Note: If possible, a sample size should be used that provides at least 1.0 mg of residue. However, due to limited sample volume, this is often not possible. If the 100 mL aliquot does not produce 1.0 mg of residue and there is sufficient sample remaining, the sample should be reanalyzed with a higher sample volume.

5.5 Turn on vacuum.

5.6 Wait till all liquid has gone through filter.

5.7 Rinse the filter with 3 10 mL portions of DI water and wait until no liquid remains on the filter.

5.8 Remove filter paper and place on drying grate being careful not to tear or damage the filter.

5.9 Place the drying grate in oven for 1 hour at 103-105^0 C.

5.10 Remove the drying grate from oven and place filters in desiccator for 1 hour to cool.

5.11 Weigh filter and residue and record weight.(B)

5.12 Redry at least 5 percent of the filters and record the redried weight. The filters must be dried to constant weight. If the difference in the redry and the original weight is greater than 0.5 mg, then all filters in the batch must be redried.

6.0 CALCULATION

(B) - (A) = weight of dried residue in mg.

$$\frac{\text{(wt. of residue in mg)}}{\text{(volume of sample in l)}} = \frac{\text{(wt. of residue in mg)x1000}}{\text{volume of sample in ml}}$$

= mg/l of residue

7.0 QC REQUIREMENTS

7.1 A method blank must be run every time the test is run.

7.2 A duplicate sample must run at least every 20 samples.

7.2 With each batch, 5 % of the samples should be redried to show that the batch has come to a constant weight.

7.2 An external reference should be run a minimum of once per quarter.

8.0 DOCUMENTATION REQUIREMENTS

8.1 Document oven temp in deg C. on worksheet before and after drying. The temperature should be measured with a thermometer that has been calibrated against a NIST traceable thermometer. All recorded temperatures should be corrected for the calibration factor.

8.2 Document start time and end time.

8.2 Document all weights and note the balance that was used.

TEST NAME: TOTAL DISSOLVED SOLIDS (TOTAL FILTERABLE RESIDUE).

LAB AREA: GN

TEST CODE: TDS

METHOD REFERENCE: EPA 160.1

DETECTION LIMIT: 10 mg/l

1.0 SCOPE AND APPLICATION

This method is used to determine the amount of solids in a sample which are capable of passing through a glass fiber filter. The method is based on EPA Method 160.1 and is applicable to all waters and wastewaters.

2.0 PRESERVATION

Water samples should be refrigerated at 4° C until analysis.

3.0 HOLDING TIME

All samples should be analyzed within 7 days of the date of collection.

4.0 INTERFERENCES

4.1 Waters containing significant amounts of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

4.2 Samples containing high concentrations of bicarbonate will require prolonged drying at 180° C to ensure that all of the bicarbonate is converted to carbonate.

4.3 Total residue in a drying dish should be limited to approximately 200 mg. If there is too much residue in a dish, water may become trapped below the residue and give an artificially high TDS number.

5.0 APPARATUS

The following items are needed for the analysis of samples following the method outlined below:

Whatman 924-AH glass fiber filters.
Filter holder with filtering flask.
100 ml evaporating dishes.
Steam baths or hot plates.
Drying oven to be set at 180° C.
Desiccator.
4-place analytical balance.

6.0 REAGENTS

Distilled water should be used for all rinsing in this method.

7.0 PROCEDURE

Below is a step-by-step procedure for the analysis of samples for TDS.

7.1 Prepare evaporating dishes by heating the clean dish to 180° C for 1 hour. Cool in desiccator and store until needed. Weigh immediately before use.

7.2 Place a clean filter in the filter holder and place the filter holder on the filtering flask. Pour three 20 ml portions of DI water through the filter. Continue to apply a vacuum to the filter until no traces of water remain. Discard the rinsing water.

7.3 Shake the sample well and measure out 100 ml in a 100 ml graduated cylinder. Turn on the vacuum.

NOTE: A smaller sample size may be used if a very high TDS value is expected. For Method Blanks, use a 100 ml portion of DI water.

7.4 Filter the sample through the glass fiber filter. Rinse with three 10 ml portions of DI water. Continue to apply a vacuum to the filter until no traces of water remain.

Rev. Date: 01/29/93
F/N GNP151.SOP
Lab Mgr: M F Cole
QA Mgr: [signature]

TEST NAME: pH by Electrode - Water

METHOD REFERENCE: EPA 150.1.

REPORTING LIMIT: not applicable

1.0 SCOPE AND APPLICATION

This method measures the pH of drinking, surface, and saline waters. This method is based on EPA 150.1.

2.0 PRESERVATION

Water samples are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and sealed tightly.

3.0 HOLDING TIME

Samples should be analyzed as soon as possible, preferably in the field or as soon as they are received by the laboratory.

4.0 INTERFERENCES

Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of greater than 10, the measured pH may be incorrectly low. For samples with a true pH of less than 1, the measured pH may be incorrectly high. In addition, temperature fluctuations and dirty electrodes can cause measurement errors. (See electrode cleaning procedure below.)

5.0 APPARATUS

The following items are needed for the analysis of pH:

5.1 pH meter with means for temperature compensation.

5.2 pH electrode.

5.3 Graduated plastic beakers.

5.4 Stir plate.

5.5 Magnetic stir bars.

5.6 Thermometer or temperature sensor for automatic compensation.

6.0 REAGENTS

All reagents listed below must be made from reagent grade chemicals.

6.1 Deionized water. This water must be monitored daily before use.

6.2 Buffer solution at pH 4, pH 7 and pH 10. Commercially available solutions that have been validated by comparison to NIST standards are recommended for routine use. All buffers must be labeled on receipt and after opening. Fresh buffer must be poured each time a new analysis is started.

7.0 PROCEDURE

Below is a detailed description of the procedure that must be followed for the determination of pH. Maker sure to properly document each step of the analysis.

7.1 Make sure that the pH electrode is clean. If the electrode is coated with oil or grease, then it must be washed with detergent and then rinse it well with DI water. Place the electrode in a beaker containing 1:10 HCL so that the lower third of the electrode is submerged and let the electrode soak for approximately 10 to 30 minutes. Then thoroughly rinse the electrode with DI water and place in a pH 7 buffer to store.

7.2 Connect the pH electrode to the pH meter. Enter the proper temperature and then calibrate the meter using two points, either pH 4 and pH 7 or pH 7 and pH 10 depending on where the pH of the samples are expected to be.

NOTE: For specific calibration procedure, see the instruction manual for the meter being used.

7.3 After the calibration is complete, analyze the 3 buffer solutions to ensure that an accurate calibration was obtained. Record the results on the pH worksheet.

7.4 Place the sample in a clean glass beaker using sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

7.5 Place the sample on the stir plate and stir. Lower the pH electrode into the solution and record the pH.

7.6 After every 10 samples have been analyzed, reanalyze one of the buffer solutions and record the result on the pH worksheet.

8.0 QC REQUIREMENTS

Below are the quality control requirement that should be followed for pH analyses on water samples. Refer to the Accutest quality control manual for additional information on quality control calculations and requirements.

8.1 A new calibration must be performed and documented each day that analysis are to be done. A pH 4, pH 7, and pH 10 solution should be analyzed immediately after the calibration is completed. The buffer checks should be within ± 5 percent of the true values.

8.2 A calibration check standard should be analyzed after every 10 samples and after the last sample analyzed in the batch. The check standard should be with ± 5 percent of the true value of the check standard solution.

8.3 A duplicate analytical sample should be analyzed for every 20 samples. The rpd for the sample and the duplicate should not exceed 10 percent.

9.0 DOCUMENTATION REQUIREMENTS

All data must be recorded on appropriate worksheets which show the results for all quality control and samples. In addition, the pH meter that was used and the buffer solutions used should be documented. All work must be dated and signed by the analyst. Any changes should be crossed
out with a single line and should be initialed and dated.

10.0 SAFETY

The analyst should follow normal safety procedures as outlined in the Laboratory Safety Manual.

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Rev. Date: 07/17/92
F/N GNP142.SOP
Lab Mgr: [signature]
QA Mgr: [signature]

TEST NAME: TCLP - VOLATILES EXTRACTION

LAB AREA: GN

TEST CODE: TCLPV (PREP ONLY)

1.0 SCOPE AND APPLICATION

The Toxicity Characteristic Leaching Procedure (TCLP) utilizes a zero-headspace extraction device to evaluate the presence and mobility of volatile organics for waste characterization.

2.0 PRESERVATION

The samples are stored at 4°C prior to extraction. The samples should be collected with no headspace. No preservatives should be added to the samples for TCLP volatile extraction.

3.0 HOLDING TIME

All volatiles must be leached within 14 days of the date of collection.

4.0 INTERFERENCES

High levels of water-miscible compounds may cause problems with quantitation and instrument contamination. Caution should be used with liquids that are not aqueous or miscible with water to avoid instrument contamination.

5.0 APPARATUS

5.1 Zero Headspace Extractor - Analytical Testing and Consulting Services, or equivalent.

5.2 Rotary Agitation Device - Analytical Testing and Consulting Services or equivalent.

5.3 Filter Holder - Millipore Corp., YT 30142HW; 142 mm.

5.4 Filter Media - Whatman GF/F; 142 mm, 0.7 um.

5.5 Glass, gas-tight syringes.

5.6 40 ml volatile vials

5.7 pH meter, reading ± 0.05 pH units.

5.8 Laboratory balance, reading ± 0.01 grams.

6.0 REAGENTS

All reagents should be prepared from reagent grade chemicals unless otherwise specified.

6.1 Organic Free Water: ASTM Type II or equivalent. Laboratory water may be boiled and sparged with helium or nitrogen for 1 hour at 95° C, if necessary to remove contaminants. Store with zero headspace in a narrow mouth bottle with teflon-lined cap.

6.2 Sodium Hydroxide, 1N. Dissolve 40 grams of sodium hydroxide in 1 liter of DI water. Mix until dissolved.

CAUTION: Solution will become warm!

6.3 Glacial Acetic Acid, Reagent Grade

6.4 Extraction Fluid; Add 5.7 ml of glacial acetic acid to 500 ml of organic free water in a 1 liter flask. A d d 64.3 ml of 1N sodium hydroxide, and dilute to 1 liter. The pH of this solution should be 4.93 ± 0.05.

7.0 PROCEDURE

7.1 Determination of percent solids. If the waste will obviously yield no liquid when subjected to pressure filtration, proceed to Section 7.3.

7.2 If the waste is a liquid or multiphasic, proceed as follows, using the pressure filtration device.

7.2.1 Pre-weigh the filter and the container that will hold the filtrate. Document all weights on the leachate form.

7.2.2 Assemble the filtering apparatus as per the manufacturer's instructions.

7.2.3 Weigh a 50-100 gram subsample of the waste and for wet sludges or 15-25 grams for soils and record the weight.

7.2.4 Quantitatively transfer the subsample to the filtering apparatus. Slurries may be allowed to settle and the liquid portion filtered prior to transferring the solid portion of the waste.

NOTE: If waste material has adhered to the sample container, obtain the weight of this residue and subtract from the total weight of the waste.

7.2.5 Complete the assembly of the filtration device, and gradually apply pressure until fluid is expelled or 10 psig is obtained. If no fluid is expelled, gradually increase the pressure in 10 psi increments to a maximum of 50 psig. If no fluid is expelled in a 2 minute period, stop the filtration. Shut off the pressurizing gas and vent the filtration system using the side port. If the pressure is taken too high and the filter breaks, start the procedure again with a new sample aliquot.

CAUTION: Do not remove flange clamps while system is pressurized! Serious injury may result!

7.2.6 The material in the filtration apparatus is defined as the solid phase.

NOTE: Some highly viscosity liquids (oils, paints) will not filter under these circumstances. The material remaining within the filtration device is defined as the solid phase.

7.2.7 Remove the solid portion of the waste sample and the filter from the filtration apparatus and weigh the filter with the solids. Determine the percent solids as shown below. It should be noted that this is a wet percent solids, and not a dry percent solids. See also section 7.2.8.

$$\% \text{ solids} = \frac{(W - F) \times 100}{T}$$

where W = weight of sample remaining on filter
F = weight of filter
T = initial weight of sample used

7.2.8 Dry the filter and solids at 100° C ± 10 to a constant weight. Record the final weight. Calculate the % dry solids using the same equation as that used in section 7.2.8.

7.2.9 If the sample contains < 5.0 percent dry solids, the filtrate is defined as the sample leachate. Proceed to Section 7.6.

7.3 Zero Headspace Extraction

7.3.1 If the waste contains < 5.0% dry solids, charge the zero headspace extractor (ZHE) with 200 ml of the sample, insert the filter and supports, and seal the vessel. Raise the piston to remove any headspace present. Attach a 50 ml glass gas tight syringe to the ZHE, and raise the piston to expel approximately 45 ml of filtrate. Transfer the filtrate to a 40 ml VOA vial with a minimum of agitation, and seal the vial. Make sure that there is no headspace in the vial. Repeat the sampling to obtain three vials of filtrate. Store at 4°C until analysis.

7.3.2 If the waste is 100% solid, weigh a 20 gram subsample and quickly transfer to the ZHE. Install the filter and supports, and seal the vessel. Measure a 400 ml aliquot (20 X sample aliquot wt) of extraction fluid into the reservoir, and attach transfer line to the ZHE. Fill the ZHE by retracting the piston with the inlet valve open. When the fluid has been transferred, remove the inlet line and raise the piston to expel any headspace. Close the valve and rotate the ZHE 2-3 times. Open the valve and expel any residual headspace. Stop at the first sign of liquid expulsion. Pressurize the ZHE to 5-10 psi, using the torque wrench supplied. Proceed to section 7.3.4.

7.3.3 If the waste is biphasic, charge the ZHE with enough sample to obtain 15-20 grams of solid using the formula shown below.

$$20\ g = \frac{x\ g\ of\ sample}{\%\ solids/100}$$

Install the filter and supports, and seal the unit. Pressurize the ZHE by raising the piston and expelling any headspace. Attach a 50 ml syringe to the ZHE and continue to raise the piston to expel the liquid phase. Transfer the liquid to 40 ml VOA vials for storage at 4°C until analysis. Charge the ZHE with extraction fluid equivalent to 20 times the sample dry weight, and pressurize the ZHE at 5-10 psi with the torque wrench provided.

7.3.4 Turn on the rotary agitator and allow the extraction to proceed for 18 $\pm$ 2 hours.

7.3.5 At the end of the extraction period, attach a 50 ml syringe to the ZHE, open the valve, and remove three 50 ml aliquots of the leachate. Transfer the aliquots to 40 ml VOA vials and store with no headspace at 4°C until analysis. If the sample has two immiscible liquids, both liquids are submitted for analysis. The results are combined mathematically after analysis according to the following formula:

$$\text{Concentration} = \frac{V_1C_1 + V_2C_2}{V_1 + V_2}$$

Where:
V_1 = Volume of first phase (liters)
C_1 = Concentration of analyte, ug/l, in first phase.
V_2 = Volume of second phase (liters)
C_2 = Concentration of analyte, ug/l, in second phase.

7.3.6 Open the ZHE and remove the remaining leachate and sample. Remove the piston and clean the vessel with hot soapy water, rinse with deionized water and dry in an oven at 110°C. (Do not bake O-rings).

7.4 Make sure that all documentation is complete and have the paperwork checked by the general chemistry lab supervisor or manager. Then make copies for the organics analysis department and distribute the sample fractions with the paperwork.

8.0 QC REQUIREMENTS

8.1 All documentation is to be done on the ZHE (TCLPV) form. Use additional pages for comments as needed. Make sure to record the extraction vessel number on the form.

8.2 A method blank should be done with every 20 extractions. A different container should be used for the method blank for each batch. The blank containers should be rotated so that all of the containers are used for a blank over time.

8.3 For each matrix type extracted, (soil, water, sludge, etc.) a leachate spike must be performed. Various unique matrices may require their own leachate spikes. Check with the lab supervisor or manager to find out the leachate volume required for a given sample. A minimum of one leachate spike must be performed for every 20 samples of a specific matrix.

9.0 SAFETY

The analyst should follow normal safety procedures as outlined in the Accutest safety manual. A labcoat and glasses should be worn for all labwork.

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Rev. Date: 07/07/92
F/N GNP141.SOP
Lab Mgr: _____
QA Mgr: _____

TEST NAME: TCLP - SEMIVOLATILES/METALS EXTRACTION

LAB AREA: GN

TEST CODE: TCLPE

1.0 SCOPE AND APPLICATION

The Toxicity Characteristic Leaching Procedure (TCLP) utilizes an extraction bottle and rotary agitation device to evaluate the presence and mobility of semi-volatile organics and metals.

2.0 PRESERVATION

The samples are stored at 4°C prior to extraction. Leachate fractions for analysis are preserved as necessary.

3.0 HOLDING TIME

Semivolatiles must be leached within 14 days of the date of collection. Mercury must be leached within 28 days of the date of collection. Metals (excluding mercury) must be leached within 180 days of the date of collection.

4.0 INTERFERENCES

Refer to the individual methods for the analytes of interest for discussion of interferences.

5.0 APPARATUS

5.1 Agitation apparatus - Analytical Testing & Consulting Services or equivalent.

5.2 Extraction Vessels - Borosilicate glass

5.3 Filtration device - Millipore Corp., YT 3014214w; 142 mm, or equivalent.

5.4 Filters - Whatman GF/F; 142 mm.

5.5 pH meter - capable of reading ± 0.05 pH units

5.6 Balance - capable of weighing ± 0.01 g

5.7 Beakers - 500 ml (or erlenmeyer flask)

5.8 Watch Glass - appropriate to cover beaker/flask

5.9 Magnetic Stirrer with stirring bars

6.0 REAGENTS

All reagents are to be prepared using ACS reagent grade chemicals unless otherwise specified.

6.1 Hydrochloric Acid, 1N; Add 83 ml of concentrated HCl to 500 ml of DI water in a 1 liter flask. Dilute to 1 liter with DI water. Mix well.

CAUTION: Perform under a hood! Irritating Vapors! Always add acids to water.

6.2 Nitric Acid, 1N; Add 64 ml of concentrated HNO_3 to 500 ml of DI water in a 1 liter flask. Dilute to volume with DI water and mix.

6.3 Sodium Hydroxide, 1N; Dissolve 40.0 grams of NaOH in 500 ml DI water in a 1 liter flask. Dilute to volume and mix.

CAUTION: The solution will become warm!

6.4 Glacial Acetic Acid, Reagent Grade

6.5 Extraction Fluids; Prepare as needed after preliminary sample evaluation. See Section 7.0.

6.5.1 Extraction Fluid #1; Add 5.7 ml of glacial acetic acid to 500 ml of DI water in a 1 liter flask. Add 64.3 ml of 1N sodium hydroxide, and dilute to 1 liter. The pH of this solution should be 4.93 ± 0.05.

6.5.2 Extraction Fluid #2: Dilute 5.7 ml of glacial acetic acid to 1 liter with DI water. The pH of this solution will be 2.88 ± 0.05

7.0 PROCEDURE

7.1 If the waste will obviously yield no liquid when subjected to pressure filtration, proceed to Section 7.3.

7.2 If the waste is a liquid or multiphasic, proceed as follows, using the pressure filtration device.

7.2.1 Pre-weigh the filter and the container that will hold the filtrate. Document all weights on the leachate form.

7.2.2 Assemble the filtering apparatus as per the manufacturer's instructions.

7.2.3 Weigh a 50-100 gram subsample of the waste and for wet sludges or 15-25 grams for soils and record the weight.

7.2.4 Quantitatively transfer the subsample to the filtering apparatus. Slurries may be allowed to settle and the liquid portion filtered prior to transferring the solid portion of the waste.

NOTE: If waste material has adhered to the sample container, obtain the weight of this residue and subtract from the total weight of the waste.

7.2.5 Complete the assembly of the filtration device, and gradually apply pressure until fluid is expelled or 10 psig is obtained. If no fluid is expelled, gradually increase the pressure in 10 psi increments to a maximum of 50 psig. If no fluid is expelled in a 2 minute period, stop the filtration. Shut off the pressurizing gas and vent the filtration system using the side port. If the pressure is taken too high and the filter breaks, start the procedure again will a new sample aliquot.

CAUTION: Do not remove flange clamps while system is pressurized! Serious injury may result!

7.2.6 The material in the filtration apparatus is defined as the solid phase.

NOTE: Some highly viscosity liquids (oils, paints) will not filter under these circumstances. The material remaining within the filtration device is defined as the solid phase.

7.2.7 Remove the solid portion of the waste sample and the filter from the filtration apparatus and weigh the filter with the solids. Determine the percent solids as shown below. It should be noted that this is a wet percent solids, and not a dry percent solids. See also section 7.2.8.

$$\% \text{ solids} = \frac{(W - F) \times 100}{T}$$

where W = weight of sample remaining on filter
F = weight of filter
T = initial weight of sample used

7.2.8 Dry the filter and solids at 100° C ± 10 to a constant weight. Record the final weight. Calculate the % dry solids using the same equation as that used in section 7.2.8.

7.2.9 If the sample contains <0.5% dry solids, the filtrate is defined as the sample leachate. Proceed to Section 7.6.

7.3 Determination of Extraction Fluid

7.3.1 Transfer a 5.0 gram aliquot of the solid phase of the sample to a 500 ml beaker.

7.3.2 Add 96.5 ml of DI water to the beaker. Place a magnetic stir bar in the beaker and cover the beaker with a watch glass. Stir vigorously for 5 min. Measure and record the pH. If the pH is <5.0, use extraction fluid #1, and proceed to step 7.4.

7.3.3 If the pH is >5.0, add 3.5 ml of 1N HCl and swirl gently. Cover the beaker with a watchglass and heat to 50° C for 10 minutes.

7.3.4 Allow the solution to cool and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2.

7.4 Extraction of Semivolatiles and metals

7.4.1 If the sample contains 100% solids, and the waste does not need size reduction (<9.5 mm), transfer a 25 to 100 g aliquot of the waste to the leaching container. Add 20 times the sample weight of the appropriate extraction fluid to the leaching container. Swirl gently and watch for the evolution of carbon dioxide. If no gasses are evolved, cap the container and mount on the rotary agitator. Allow the extraction to proceed for 18 $\pm$ 2 hrs. The vessels should be vented periodically to prevent pressure build up. Proceed to section 7.5.

7.4.2 If the waste contains <0.5% solids, then filter sufficient sample for all of the scheduled leachate tests. The filtrate is defined as the leachate.

7.4.3 If the waste is mixed phases, transfer a 100g aliquot of the waste to the filtration device. Assemble the filtration apparatus, and gradually apply pressure to remove any free liquids. Expelled liquid is stored in a glass container, and is to be recombined with sample leachate. Transfer the solid portion of the waste to a pre-weighed leaching bottle. Weigh the bottle with the sample and subtract the weight of the sample to obtain the total weight of solid added. Add a volume of the appropriate leaching fluid equal to 20 times the weight of the solid to be leached. Swirl gently and watch for evolution of carbon dioxide. Cap the extraction bottle and attach to rotary agitator. Allow the extraction to proceed 18 $\pm$ 2 hrs.

NOTE: If the sample contains a very low % solids, more sample can be filtered to obtain sufficient solids for leaching such that all analyses may be performed.

7.5 After the leaching period has elapsed, remove the containers from the rotary agitator. Assemble the filtration device. Filter the extract, and if a compatible liquid was obtained in Section 7.4.3, combine the liquids at this time. If the liquids are not compatible, submit both fractions for analysis.

The results for non-compatible fractions are combined mathematically after analysis according to the formula:

$$\text{Concentration} = \frac{V_1C_1+V_2C_2}{V_1+V_2}$$

Where:
- V_1 = Volume of first phase (liters)
- C_1 = Concentration of analyte, ug/l, in first phase.
- V_2 = Volume of second phase (liters)
- C_2 = Concentration of analyte, ug/l, in second phase.

7.6 Once the filtrate has been collected and combined, record the pH on the leachate form, and aliquot the leachate for the necessary analyses.

7.7 Add nitric acid to a small fraction (approx. 10 ml) of the leachate and check for precipitation. If there is no precipitation, then preserve the metals fraction only of the leachate with nitric acid to a pH of less than 2.0. Make sure not to preserve the organics fractions of the sample.

7.8 Make sure that all documentation is complete and have the paperwork checked by the general chemistry lab supervisor or manager. Then make copies for the appropriate departments (extractions or metals) and distribute the sample fractions with the paperwork.

8.0 QC REQUIREMENTS

8.1 All documentation is to be done on the TCLP form. Use additional pages for comments as needed. Make sure to record the extraction vessel number on the form.

8.2 A method blank should be done with every 20 extractions. A different container should be used for the method blank for each batch. The blank containers should be rotated so that all of the containers are used for a blank over time.

8.3 For each matrix type extracted, (soil, water, sludge, etc.) a leachate spike must be performed. Various unique matrices may require their own leachate spikes. Check with the lab supervisor or manager to find out the leachate volume required for a given sample. A minimum of one leachate spike must be performed for every 20 samples of a specific matrix.

9.0 SAFETY

The analyst should follow normal safety procedures as outlined in the Accutest safety manual. A labcoat and glasses should be worn for all labwork.

Manager:
QAO:

Title: Air Analysis of Tedlar Bag or Summa Canister by TO-14

1.0 SCOPE AND APPLICATION

This method is for the analysis of volatile and semivolatile organics on whole ambient air samples collected in Tedlar bags or summa canisters.

2.0 METHOD REFERENCES

2.1 USEPA METHOD TO-14 "Methods for the Determination of Toxic Organic Compounds in Air", 1990

2.2 USEPA SW846 8240, 3rd edition, "Volatile Organics by GC/MS"

3.0 METHOD SUMMARY

3.1 A whole air sample collected in a summa passivated canister or Tedlar bag is concentrated by adsorption and cryofocusing and introduced into a GC/MS for target compound analysis.

3.2 The GC/MS is calibrated with a 5 level curve with quantitation performed by internal standard technique. Standards are purchased as commercial gas standards or prepared by static dilution technique by the laboratory.

3.3 A typical sample volume of 400cc is drawn out of a pressurized or ambient canister or Tedlar bag and trapped on a glass bead trap, tenax trap and cyrofocused prior to introduction into the GC/MS.. The GC oven is temperature programmed to separate the compounds of interest with detection by a mass selective detector.

3.4 This method is applicable to the compounds listed on Table 5.

3.5 The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The RDL (Reporting Detection Limit) for an individual compound is listed on Table 5.

4.0 HOLDING TIME

4.1 48 hours for Tedlar bag.

4.2 14 days for summa canister.

4.3 Summa Canisters and Tedlar Bags are stored at ambient temperature.

5.0 INTERFERENCE'S

5.1 High CO2 samples such as landfill gas may freeze and restrict flow on the traps causing reduced sample volume.

5.2 Common laboratory solvents such as methylene chloride, acetone, and Freon 113.

6.0 APPARATUS

6.1 Hewlett Packard 5890 series II GC with 5971 MSD.

6.2 PC based Hewlett Packard chemstation with Enviroquant software.

6.3 Entech model 7016CA 16 position canister autosampler.

6.4 Entech model 7000 preconcentrator.

6.5 Entech model 4560SL Dynamic Standards Diluter equipped with a 5000 sccm (for dilution gas) and 50sccm (for standard) flow controllers.

6.6 30psig to 30" Hg vac pressure gauges.

6.7 0-60psig pressure gauge for summa canister pressurization.

6.8 6 liter certified (see canister cleaning SOP) passivated summa canisters or silocans evacuated to under 0.05mm Hg.

6.9 Hewlett Packard packed injection port externally mounted for adaptation to summa canister.

6.10 0.1cc, 0.5cc, 1cc, 5cc, 10cc, 50cc gas tight syringes with point #5 style needles.

6.11 Heating band fixed at 100c to encompass diameter of summa canister.

6.12 Various swagelok fittings.

6.13 Syringe adapters for summa canisters if manual injection or dilution needed.

7.0 STANDARDS AND REAGENTS. The manufacturer brands listed may be substituted with equivalent standards.

7.1 Protocol neat Cocktail Standards Mix Certified @ > 99% purity. Each compound at equal molar weight.

Standards

- Acetone
- Methyl tert butyl ether
- Carbon Disulfide
- 1,3-butadiene
  - Vinyl Acetate
- 4-Methyl-2-Pentanone
- Benzyl Chloride
- 2-Hexanone
- 2-Butanone
- Bromodichloromethane
- dibromochloromethane

Surrogates Standard

- 4-bromofluorobenzene

Internal Standards

- Bromochloromethane
- 1,4-Difluorobenzene
- Chlorobenzene-d5

7.2 Scotty IV certified 1ppmv TO-14 stock standard.

7.3 Restek certified 1ppmv TO-14 stock standard (Matheson Gas supplier for Restek).

7.3 Reagent grade organic free water.

7.4 Zero grade gases:

- Helium
- Nitrogen Dewar
- Zero air

8.0 STATIC DILUTION STANDARD PREPARATION

8.1 Static Dilution Cocktail Mix

8.1.1. Equal weighing factors based on molecular weight and density is used for each compound

8.1.2. ***Calculation*** :the amount of each standard is determined by approximating a transfer volume such as 500ul for each compound which would give us a total volume of 5-6 ml. The actual amount of each compound will be (500) x (density)/ (MW). Therefore acetone would be (500) x(0.791)/ (58) or 367 ul in the standards cocktail mix.

8.1.3. If standard cocktail mix is not commercially available, the mix would be prepared as follows;

Volumes of each solvent is transferred into a 10ml vial utilizing a 1000ul syringe. If dedicated syringes are not available, rinsing should be performed with the standard itself and expelling into a waste vial. Waste vials are disposed into the appropriate waste drum.

Calibration Standard Cocktail:

• Acetone	367 ul
• Methyl tert butyl ether	676 ul
• Carbon Disulfide	300 ul
• 1,3-butadiene	416 ul
• Vinyl Acetate	461 ul
• 4-Methyl-2-Pentanone	626 ul
• Benzyl Chloride	575 ul
• 2-Hexanone	617 ul
• 2-Butanone	447 ul
• Bromodichloromethane	414 ul
• dibromochloromethane	425 ul

Internal Standard Cocktail

- Bromochloromethane 320 ul
- 1,4-Difluorobenzene 510 ul
- Chlorobenzene-d5 530 ul

Surrogate Standard Cocktail

- 4-Bromofluorobenzene neat

8.2 Standard summa canister configuration for static dilution standards

8.2.1 A 6 liter evacuated summa canister (<0.050mm Hg) is equipped with a Hewlett Packard packed injection port wired externally to an unused injection port control of the GC/MS. This way the temperature can be controlled by the front GC/MS keyboard panel.

8.2.2 Helium is plumbed to the carrier line of the injection module and set to about 60psi with an adjustable flow gauge which measured approximately 40ml/min.

8.2.3 The injection port is fitted with a 1/4" female swagelok connector and attached to the a summa canister 1/4" male sampling port.

8.2.4 The canister is wrapped with a heating band supplied with the Entech model 3000 canister cleaning apparatus which heats to 100c near the base. The injection port is heated to 80 C by the injection port control on the GC.

8.2.5 Turn on the helium gas flow a well as the canister valve to start drawing under vacuum.

8.3 Standard introduction into canister

8.3.1 Inject 200ul of reagent grade water through the septa of the injection module to secure any active sites. The appropriate amount of standard cocktail mix and gas is injected with the canister drawing heluim and remain heated for about 30 minutes.

The canister is pressurized to 15psig with helium and allowed to cool to ambient temperature.

8.3.2 10 ppmv stock standard calibration standard

- Inject 12 ul of standard cocktail into summa injection. The canister is pressurized while still warm to about 20psig to enhance compound stability. Once the canister is cooled the canister is pressurized to 30psig or an equivalent final volume of 18liters.

10ppbv working calibration standard - refer to **section 9** for complete calibration standard

8.3.3 50 ppmv internal/ 25ppmv surrogate stock standard

- Inject 10ul of internal cocktail, 2ul of BFB standard to 30psig final canister pressure

8.3.4. 40ppbv internal/ 20ppbv surrogate working standard

- dilution stream attached to a evacuated 6 Liter canister to Introduce 24 cc of stock standard (**section 8.3.3**.)into final pressure of 15psig
- This pressurized canister allows for several standard aliquots to be injected along with compound stability.

9.0 DYNAMIC DILUTION STANDARD PREPARATION

9.1 10ppb Calibration Standard

9.1.1 Allow Entech 4560SL to warm up for 15 minutes.

9.1.2 The nitrogen vent line is plumbed through a canister equipped with dip tube containing 300ml of deionized water to humidify the dilution gas. Attach this utilizing a 1/4" flushed copper tube to Mass Flow Controller (MFC) port 1. The vent gas on a Nitrogen dewar is approximately 35 psig.

9.1.3 A 1ppmv calibration gas is attached to MFC port 2 and set at 50 psig head pressure to allow for the proper pressure differential.

9.2 From the software control, enter the calculated mass flow controller values which is 2500sccm for MFC1 or dilution gas and 25sccm for MFC2 or standard. This is a 1:100 dilution blend to result in a 10ppbv working calibration standard.

9.3 Open the isolation valve and let gasses purge for a few minutes.

9.4 Add 100ul of deionized water to port of clean evacuated canister to deactivate any sites.

9.5 Attach pressure sensor canister fill line with a "TEE" to the canister port and tighten. The "tee" configuration is used to introduce the static dilution standard of extra target compounds already prepared in **section 8.3.2.**

9.6 Select "go" on the software control and open canister to begin filling. Notice the pressure sensor reading in psia on the software control drops dramatically to correspond with the high vaccum of the prepared canister.

9.7 While filling, add 10cc of the 10 ppmv dilution standard. This amount is calculated to obtain a 1:1000 dilution for a final volume of 10 liters. To obtain a volume of 10 liters the 6 liter canister should have a final pressure of 24.5 psia.

24.5psia/14.7psia x 6 liters = 10 liters

Therefore when adding this additional standard, the canister valve must be turned off when the pressure sensor reads 24.5 psia.

9.8 *Laboratory Control Standard (LCS)*

9.8.1 Scotty TO-14 standard is prepared the same as the Restek cal standard but the static dilution standard is not added and the final pressure does not have to be monitored. An LCS is used to verify calibration with a second or external source standard.

9.9 ***Method Blank***

9.9.1 A 6 liter evacuated canister is filled and pressurized to 15 psig with zero grade helium nitrogen or a nitrogen gas line is attached to an autosampler port with about 5psig pressure.

10.0 SUMMA CANISTER SHIPPING AND RECEIVING

10.1 Canister Shipping

10.1.1 Record prepared certified summa canister (Refer to SOP) and vaccum in canister log book.

10.1.2 For integrated sampling, a canister must be equipped with a clean calibrated attached or detached flow controller.

10.1.3 The flow controller is calibrated by forcing zero grade nitrogen at 5-10psig through the flow controller and adjusting the flow control calibrator while measuring the flow in cc/min with a flow meter.

10.1.4 Ideally approximately some vaccum should remain in canister after sampling for more stability. Therefore measure the flow over the specified sampling period to fill the canister with about 5 liters of air. This would leave a vaccum of about 5" Hg.

10.1.5 For a 24 hour sample this would be 5000cc/ (60min)(24 hr) or 3.5cc/min.

10.1.6 A grab sample is a summa canister without any flow controller and takes about 20 seconds to fill.

10.2 Canister Receipt

10.2.1 Upon receipt of the canister, the pressure or vacuum should be checked to ensure proper sampling was performed. If excessive vacuum (>10" Hg) or absence of vacuum (0psig, 0"Hg) is measured the client should be notified to inquire about a shortened sampling or a lengthened sampling period.

10.2.2 The pressure or vacuum along with received date and lab sample # should be recorded in the canister log book.

11.0 INSTRUMENT CONDITIONS

11.1 *Entech Autosampler/ Concentrator conditions*

11.1.1 7016CA autosampler — Valve 80°C; Transfer Line 80°C

11.1.2 7000 Concentrator

		Internal Standard		Sample Sweep
Preflush sec	5	15	15	2
Trap cc/min	100	150	150	100
Volume 100		varies	400	75

	Trap	Preheat	Desorb	Bake
Module 1	-150 °C	20 °C	20 °C	130 °C/ 5 min
Module 2	-10 °C	no	180 °C	190 °C/ 3.5 mi
Module 3	-160 °C	100 °C	2min	100 °C/ 2min

GC/MS Transfer line 100 °C

Total event cycle time 40 min

11.2 *GC Conditions*

11.2.1 Hewlett Packard 5980 gas chromatograph

11.2.2 Column - J&W 60 meter DB-624, 0.32mm id, 1.8 um film thickness.

11.2.3 Helium carrier gas at approx. 12psig column head pressure.

11.2.4 GC Temperatures:

injection port	120 °C
detector	280 °C
oven	50 °C held for 4min
	12 °C /min to 260 °C and held for 1.0min

Total runtime 22.5 min

Electronic Pressure Control:	15psi for 0.3 min
	99psi/ min to 7psi for 0min
	Vacuum Comp On
Purge Valve	Off at 1.00 min

11.3 Mass Spectrometer Conditions

11.3.1 Hewlett Packard 5971 MSD.

11.3.2 Capable of scanning from 35-300 amu every 3.8 second or less utilizing a 70 volt (nominal) electron energy in the electron impact ionization mode.

11.3.3 Threshhold at 400 with a solvent delay of 4.2 min.

11.3.4 Capable of producing a mass spectrum which meets all the criteria in Table 1 when injecting 100cc of 5ppbv Bromofluorobenzene(BFB).

11.4 Data System

11.4.1 A computer system is interfaced to the mass spectrometer which allows for continuous acquisition and storage on machine readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

11.4..2 The computer utilizes software which allows searching any GC/MS data file for target analytes which display specific fragmentation patterns.

11.4.3 The HEWLETT PACKARD ENVIROQUANT (PC) data system is capable of quantitation using multipoint calibration and multipoint internal standards.

11.4.4 The recent version of the EPA/NBS mass spectral library (54,000 compounds) is being used for non target peak tentative identification.

11.4.5 Data is archived through the network server to centralized hard drive.

12.0 ANALYSIS

12.1 Daily BFB system performance tuning.

12.1.1 The 40ppbv internal standard and 20ppbv surrogate is attached to the internal standard port of the Entech 7000 utilizing flushed 1/8" copper tubing.

12.1.2 100cc of this standard will be sampled which is equivalent to 5ppbv of BFB.

12.1.3 The GC/MS and Entech concentrator conditions will be the same as in section 11 with the sample amount and standard amount set to "0"

12.1.4 Once the tune is complete, a spectra of the BFB peak must be checked to verify acceptable performance criteria are achieved (see Table 1)

12.1.5 This performance test must be passed before any samples, blanks or standards are analyzed.

12.1.6 If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are met.

12.1.7 The injection time of the acceptable tune analysis, is considered the start of the 24 hour clock.

12.2 Initial Calibration

12.2.1 A 5 or 6 level calibration is performed utilizing 0.5, 1, 5, 10, 20, 40 ppbv for all compounds.

12.2.2 The 10ppbv calibration standard is attached to the standards port on the Entech 7000 utilizing flushed 1/8" copper tubing

12.2.3 Considering a normal volume of 400cc, the volumes of a 10ppbv standard will be 20,40,200,400,800,1600cc to be equivalent to 0.5, 1.0, 2.0, 5.0, 10, 20 , and 40 ppbv.

12.2.4 The internal standard/ surrogate volume will be 100cc for all standards, samples and quality control resulting in a 10 ppbv internal standard and 5 ppbv surrogate standard concentration.

12.2.5 The linear range covered by this calibration is highest concentration standard.

12.2.6 Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 4.

12.2.7 The Response Factor (RF) is calculated for each compound at every standard level.

Response Factor (RF)

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

where: As = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cs = Concentration of the compound being measured (ppbv).
Cis = Concentration of the specific internal standard (ppbv).

12.2.8 Percent Relative Standard Deviation (% RSD) is calculated for all calibration levels used.

$$\%RSD = \frac{SD}{RFav} \times 100$$

where: SD = Standard Deviation
RFav = Average response factor from initial calibration.

12.2.9 The following criteria must be met for the initial calibration to be valid.

- The percent relative standard deviation must be less than 30 %.
- Up to two compounds may exceed 30% but must be less than 40% for a valid initial calibration.

12.3 Continuing calibration

12.3.1 A continuing calibration check standard at the 5ppbv concentration must be acquired every 24 hrs which is equivalent to 200 cc of the 10 ppbv standard

12.3.2 The percent difference for all continuing calibration compounds must be less than 30.

Percent Difference (%D).

$$\%D = \frac{(Cq - Cc)}{Cq} \times 100$$

where: Cq = Calibration Check Compound standard concentration.
Cc = Measured concentration using selected quantitation method.

12.3.3 If either of the criteria fail, a new five point calibration must be performed.

12.4 Internal Standard

12.4.1 100 cc of the internal/ surrogate standard is equivalent to 10ppbv which is added to all standards, samples and QC.

12.4.2 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or retention time changes by more than 30 seconds from the last daily calibration check standard or the 5 ppbv level of the initial calibration, the mass spectrometer must be inspected for malfunctions and corrections will be made, as appropriate.

12.5 Method Blank

12.5.1 400cc of zero grade nitrogen **(section 9.9)** is analyzed prior to any samples and should be non-detect for all target compounds. Occasionally lab background such as Freon 113 cannot be fully eliminated and should be flagged appropriately in any samples.

12.6 Sample analysis - General

12.6.1 Typically a 400 cc sample volume is standard for analysis to achieve a 0.2ppbv detection limit. Smaller sample amounts down to 20 cc can be sampled accurately with the concentrators mass flow controller.

12.6.2 Further dilution's can be performed by utilizing a gas tight syringe to inject smaller volumes into a nitrogen stream attached to one of the autosampler ports with a "TEE" configuration with septa. The sample size can be software designated as 100 cc with the actual sample being injected into this 100 cc nitrogen stream during the sampling step.

12.7 Tedlar bag sample analysis

12.7.1 Sample must be injected within 48 hours of sample collection

12.7.2 The Tedlar bag is attached to the sampling port using a 1" length of flexible Teflon tubing with proper inside diameter to create a tight seal with the Tedlar bag.

12.8 *Summa canister sample analysis*

12.8.1 Canister pressure should be checked and recorded upon receipt by the laboratory as in section 10.2.

12.8.2 The canister may be pressurized upon receipt for screening purposes or if excessive vacuum remains at receipt (<10 " Hg). If the canister is pressurized, the sampling volume must be adjusted to compensate for the dilution. A 2-fold dilution of the summa canister would result in sampling 800 cc for a 0.2 ppbv detection limit.

12.8.3 Typically a two fold dilution is adequate which is calculated as psia *final/psia received where psia = pounds per square inch absolute.*

As an example a canister is received under slight vacuum at 5" Hg;

0.4912 x 5 = 2.456 psia(vac)

14.7 psia(ambient) - 2.456(vac) = 12.24 psia received

12.24 psia x 2 = 24.5 psia final for two fold dilution

24.5 psia(final) - 14.7 = 9.8 psig final

13.0 *DATA INTERPRETATION*

13.1 Qualitative identification.

The targeted compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The criteria required for a positive identification are:

13.1.1 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criteria is the RRT of sample component must be within ± 0.06 RRT units of the standard.

13.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10 % (major abundant ion in the spectrum equals 100 %) should be present in the sample spectrum.

13.1.3 The relative intensities of these ion must agree within ± 30 % between the daily standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 20 and 80 %.

13.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficiently GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 % of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13.2 Quantitative analysis

13.2.1 When a target compound has been identified, concentration (see section 15.1) will be based on the integrated area of the quantitation ion, normally the base peak (see Table 4).

13.2.2 If the sample produces an interference for the primary ion, use a secondary ion to quantitate (see Table 4). This is characterized by an excessive background signal of the same ion which distorts the peak shape beyond a definitive integration. Also an interference could severely inhibit the response of the internal standard ion. This secondary ion must also be used to generate new calibration response factors.

13.3 Library search for tentatively identified compounds.

If a library search is requested, the analyst should perform a forward library search of NBS mass spectral library to tentatively identify 15 non-reported compounds. Guidelines for making tentative identification are listed below.

13.3.1 These compounds should have a response greater than 10 % of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

13.3.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

13.3.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

13.3.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) should be present in the sample spectrum.

13.3.5 The relative intensities the major ions should agree within ± 20 %.

13.3.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

13.3.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

13.3.8 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

13.3.9 Quantitation will be performed on the nearest internal standard.

14. QUALITY CONTROL

QC Requirements Summary:

BFB	Every 24 hrs.
Calibration Check std	Every 24 hrs.
Batch blank	Every 24 hrs.
Matrix Duplicate	one per 20 samples
Lab Control Sample (LCS)	one per 20 samples
Surrogate	every sample and standard.
Internal Standard	every sample and standard.

14.1 Daily GC/MS performance check - refer to section 12.1.

14.2 Daily calibration check - refer to section 12.3.

14.3 Method blank (reagent grade nitrogen) at 400 cc - refer to section 12.5.

14.4 Matrix Duplicate.

14.4.1 One sample is selected at random. The Relative Percent Difference (see section 15.3) should be calculated for all hits. See Table 5 for criteria.

14.5 Laboratory Control Sample (LCS). An external source standard.

14.5.1 Laboratory Control Standard (LCS) is prepared to contain 10 ppbv each analyte from a source other than the calibration standard. 200 cc of the LCS is sampled for a 5ppbv.

14.5.2 Percent recoveries (% R) (see section 15.2) are compared the limits on Table 5. At least 75% of the compounds should be within control limits. **Note**: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 2SP.

14.5.3 If laboratory control samples do not meet criteria, calculations should be checked. A new LCS should be prepared and analyzed and possibly a new calibration if the problem isn't rectified.

14.6 Surrogate

14.6.1 All blanks, samples, and matrix spikes contain surrogate compounds which are used to monitor method performance. All samples are spiked with 100cc of the internal/surrogate standard which is equivalent to 5ppbv of 4-Bromofluorobenzene.

14.6.2 If the % recovery (see section 15.2) of 4-Bromofluorobenzene does not meet the control limits specified in Table 3, the recovery must be flagged and:

14.6.2.1 The calculation must be checked.

14.6.2.2 The sample may be reanalyzed if the recovery of the surrogate is out of control limit without any apparent matrix interference.

14.6.3 Reanalysis is not required for samples exhibiting matrix interference, defined as excessive signal levels from target and non-target interfering peaks.

14.6.4 If surrogate recoveries are acceptable upon reanalysis, the data from the reanalysis is reported. If the reanalysis date did not meet the hold time, then both sets of data have to submitted with the reanalysis reported.

14.6.5 If surrogates are still outside control limits upon reanalysis, then both sets of data should be submitted with the first analysis reported.

Note: As database records become available, method accuracy will be assessed by calculating average percent recovery (AVE %R) and the standard deviation (SP) of recovery to express control limits as AVE %R +/- 3SP.

14.7 Internal Standard.

14.7.1 Retention time for all internal standard must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 100 ug/l standard of initial calibration.

14.7.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area in the latest calibration standard (24 hr. time period).

14.7.3 If area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

14.7.4 If areas are acceptable upon reanalysis, the reanalysis data is reported.

14.7.5 If areas are unacceptable upon reanalysis, then both set of data are submitted with the original analysis reported.

15. CALCULATIONS

15.1 Concentration (Conc.)

$$\text{Conc. (ug/l)} = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Vi}$$

Where: Ac = Area of characteristic ion for compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cis = Concentration of the specific internal standard (ug/l).
Vp = 400cc (Standard Volume)
RF = average response factor from initial calibration
Vi = volume of sample (cc).

15.2 Percent Recovery (% R)

$$\%\ R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

15.3 Relative Percent Difference (RPD)

$$RPD = \frac{|SC - SDC|}{(1/2)(SC+SDC)} \times 100$$

Where: SC = Sample Concentration
SDC = Sample Duplicate Concentration

16.0 DOCUMENTATION.

16.1 The Analytical Logbooks records the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

16.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in the comments section

16.2 The Standards Preparation Logbook must be completed for all standard preparations. All information must be completed, the page must be signed and dated by the appropriate person.

16.2.1 The Accutest lot number must be cross referenced on the standard vial.

16.3 Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

17.0 APPARATUS CLEANING

17.1 Sample syringes and canister syringe adapters are cleaned between use by baking at 50 C for 20 minutes. Higher temperatures can crack the barrel of the fixed needle syringe. The syringes and adapters are also flushed with the actual sample prior to final aliquot injection.

17.2 Summa canisters are cleaned and certified (refer to SOP GCSUMMA.)

18.0 SAFETY

18.1 All standard preparation must be performed under a ventilation hood.

18.2 Releasing pressurized summa canisters must be performed under a ventilation hood.

18.3 Analysts must follow safety guidelines specified in Accutest's Chemical Hygiene Plan.

Table 1

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15-40 of mass 95
75	30-60 of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 198
175	5-9% of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Table 2

INTERNAL STANDARD IONS

Internal Standard	Prim/Sec. Ions
Bromochloromethane	128 / 49, 130, 51
1,4-Difluorobenzene	114 / 63,88
Chlorobenzene-d5	117 / 82, 119

Table 3

SURROGATE CONTROL LIMITS

Compound	(Prim/Sec. ions)	% Recovery
4-Bromofluorobenzene	(95 / 174, 176)	80-120

Table 4

TARGET COMPOUND IONS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Acetone	58	43
Benzene	78	-
Benzyl chloride	91	91, 126, 65, 128
Bromobenzene	156	77, 158
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
2-Butanone	72	43, 72
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chlorodibromomethane	129	208, 206
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
Dichlorodifluoromethane	85	87
1,1-Dichlorethane	63	65, 63
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63

Table 4 -continued

TARGET COMPOUND IONS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
cis-1,2-Dichloroethene	96	61,98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
Ethylbenzene	91	106
Freon 113	151	101, 103
Freon 114	85	135, 87
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	142, 127, 141
4-Methyl-2-pentanone	100	43, 58, 85
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91

Compound	RDL	RDL	LCS Limits	RPD
	ppbv	ug/m3	%	%
Benzene	0.20	0.64	60-140	30
Bromomethane	0.20	0.77	60-140	30
Benzyl Chloride	0.20	1	60-140	30
Chlorobenzene	0.20	0.92	60-140	30
Chloroethane	0.20	0.52	60-140	30
Chloroform	0.20	0.96	60-140	30
Chloromethane	0.20	0.41	60-140	30
Carbon Tetrachloride	0.20	1.2	60-140	30
1,2-Dichloroethane	0.20	0.8	60-140	30
1,1-Dichloroethylene	0.20	0.78	60-140	30
1,2-Dibromoethane	0.20	1.5	60-140	30
1,2-Dichloroethane	0.20	0.8	60-140	30
1,2-Dichloropropane	0.20	0.92	60-140	30
Dichlorodifluoromethane	0.20	0.98	60-140	30
cis-1,2-Dichloroethylene	0.20	0.78	60-140	30
cis-1,3-Dichloropropene	0.20	0.9	60-140	30
m-Dichlorobenzene(1,3)	0.20	1.2	60-140	30
o-Dichlorobenzene(1,2)	0.20	1.2	60-140	30
p-Dichlorobenzene(1,4)	0.20	1.2	60-140	30
trans-1,3-Dichloropropene	0.20	0.9	60-140	30
Ethylbenzene	0.20	0.87	60-140	30
Freon 113	0.20	1.5	60-140	30
Freon 114	0.20	1.4	60-140	30
Hexachlorobutadien	0.20	2.1	60-140	30
Methylene Chloride	0.20	0.69	60-140	30
MTBE	0.20	0.82	60-140	30
Styrene	0.20	0.85	60-140	30
1,1,1-Trichloroethane	0.20	1.1	60-140	30
1,1,2,2-Tetrachloroethane	0.20	1.4	60-140	30
1,1,2-Trichloroethane	0.20	1.1	60-140	30
1,2,4-Trichlorobenzene	0.20	1.5	60-140	30
1,2,4-Trimethylbenzene	0.20	0.98	60-140	30
1,3,5-Trimethylbenzene	0.20	0.98	60-140	30
Tetrachloroethylene	0.20	1.3	60-140	30
Toluene	0.20	0.75	60-140	30
Trichloroethylene	0.20	1.1	60-140	30
Trichlorofluoromethane	0.20	1.1	60-140	30
Vinyl Chloride	0.20	0.51	60-140	30
m,p-xylene	0.20	0.87	60-140	30
o-xylene	0.20	0.87	60-140	30
Xylene(total)	0.20	0.87	60-140	30

RDL - Reporting Detection Limit.
LCS - Laboratory Control Sample.
RPD - Relative Percent Difference.

APPENDIX 12.2

SEPTEMBER 13, 1996 SSIPL CONFIRMATION LETTER

CRA

CONESTOGA-ROVERS & ASSOCIATES
651 Colby Drive
Waterloo, Ontario, Canada N2V 1C2
(519) 884-0510 Colby Office Fax: (519) 884-0525
(519) 725-3313 Bathurst Office (519) 725-1394

September 13, 1996

Reference No. 6029-50

Mr. Anthony Rutter
Director, Waste Management Division
Remedial Project Manager
U.S. Environmental Protection Agency
77 West Jackson Boulevard
Chicago, IL 60604

Mr. Regan S. Williams
State Project Coordinator
Ohio EPA - Division of
Emergency & Remedial Response
2110 East Aurora Road
Twinsburg, OH 44087

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Gentlemen:

Re: Groundwater Monitoring
Summit National Superfund Site
Deerfield, Ohio

This letter summarizes the Site-specific Indicator Parameter List (SSIPL) and revised groundwater monitoring requirements for the Summit National Superfund Site (Site) in Deerfield, Ohio as discussed during the conference call on September 5, 1996. The SSIPL for the Site will be as follows:

SSIPL Volatile Organic Compounds (VOCs)

Acetone
1,1-Dichloroethane
1,2-Dichloroethane
Ethylbenzene
Toluene
Xylene
Trichloroethylene
1,2-Dichloroethylene
2-Butanone (MEK)

SSIPL Semi VOCs (SVOCs)

Phenol
4-Methylphenol
2,4-Dimethylphenol
2-Methylphenol
Isophorone

SSIPL Metals

Cadmium
Lead
Nickel

The groundwater monitoring schedule with associated analytical parameters will be as follows:

Sampling Date	*Monitoring Wells*	*Analytical Parameter*
November 1996	WTU, UIU, LIU, and USU[1]	SSIPL VOCs and Metals
May 1997	WTU, UIU, and LIU	SSIPL VOCs and Metals
November 1997	WTU, UIU, LIU, USU, and Residential Wells	SSIPL VOCs, Metals, and SSIPL SVOCs (select wells only)
May 1998	WTU, UIU, and LIU	SSIPL VOCs and Metals
November 1998	WTU, UIU, LIU, and USU	SSIPL VOCs and Metals
May 1999	WTU, UIU, and LIU	SSIPL VOCs and Metals
November 1999	WTU, UIU, LIU, USU, and Residential Wells	Full TCL/TAL[2]

Note: (1) WTU - Water Table Unit
UIU - Upper Intermediate Unit
LIU - Lower Intermediate Unit
USU - Upper Sharon unit
(2) TCL - Target Compound List
TAL - Target Analyte List

A re-evaluation of the SSIPL and groundwater monitoring schedule will be made following the November 1999 groundwater sampling event.

The following monitoring wells for which samples will be analyzed for the SSIPL SVOCs during the November 1997 sampling event are proposed for approval by the United States Environmental Protection Agency (USEPA) and the Ohio Environmental Protection Agency (OEPA):

September 13, 1996 Reference No. 6029-50

Aquifer	*Wells*	*Comments*
WTU[1]	MW-11	On Site
	MW-102	North of Site, Background Well
	MW-103	West of Site, Background Well
	MW-107	On Site
	MW-108	On Site
	MW-110	East of Site
	MW-115	South of Site
UIU[2]	MW-202	North of Site
	MW-204	Southwest of Site, Background Well
	MW-205	South of Site, Background Well
	MW-207	On Site
	MW-209	East of Site, Downgradient Well

Notes: (1) Horizontal direction of groundwater flow is southeasterly.
(2) Horizontal direction of groundwater flow is easterly.

As no SSIPL SVOC's have been detected in the UIU, LIU or the USU, it has been proposed to analyse for SSIPL SVOC's in the WTU and UIU only. We trust the above revised groundwater monitoring schedule is acceptable to USEPA and OEPA.

Should you have any questions, please do not hesitate to contact the undersigned.

Yours truly,

CONESTOGA-ROVERS & ASSOCIATES

[redacted], P. Eng.

SW/dm/34
c.c.: Richard McAvoy
Gary Gifford
Patrick Steerman
Kenneth Walanski
Jack Michels
Richard Murphy

Rec'd CRA

OCT 11 1996

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

OCT 10 1996

REPLY TO THE ATTENTION OF:
SR-6J

Mr. Steve Whillier
Conestoga Rovers & Associates Limited
8615 W. Bryn Mawn Avenue
Chicago, Illinois 60631

Dear Mr. Whillier:

We have reviewed the September 13, 1996 letter which summarizes the Site-specific Indicator Parameter List (SSIPL) and revised groundwater monitoring requirements for the Summit National site. We find that the proposed changes are acceptable and we are approving the O&M plan when these changes are made.

If there are any questions please contact me at (312) 886-8961.

Sincerely,

Anthony J. Rutter
Remedial Project Manager

cc: Gary Gifford
Regan Williams

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OhioEPA
State of Ohio Environmental Protection Agency
Northeast District Office
110 E. Aurora Road
Twinsburg, Ohio 44087-1969
(216) 425-9171
FAX (216) 487-0769

Rec'd CRA

OCT 21 1996

George V. Voinovich
Governor

October 18, 1996

RE: SUMMIT NATIONAL
PORTAGE COUNTY
OHIO ID # 267-0779

Mr. Steve Whillier
Conestoga Rovers & Associates, Ltd.
8615 West Bryn Mawn Avenue
Chicago IL 60631

Dear Mr. Whillier:

We have reviewed you letter dated 9/13/96, regarding the Site Specific Indicator Parameter List for the Summit National Site. We find that the proposal addresses all of the concerns raised by Ohio EPA on our 9/5/96 conference call, and is therefore acceptable.

Please feel free to call me at (216) 963-1210 should you have any questions about this letter.

Sincerely,

Regan S. Williams
Environmental Specialist
Division of Emergency and Remedial Response

RSW:ddb

cc: Rich Kurlich, DDAGW

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